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Monte Carlo Studies of Systems of Hard Spheres

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October 1, 1964

Courant Institute of Mathematical Sciences

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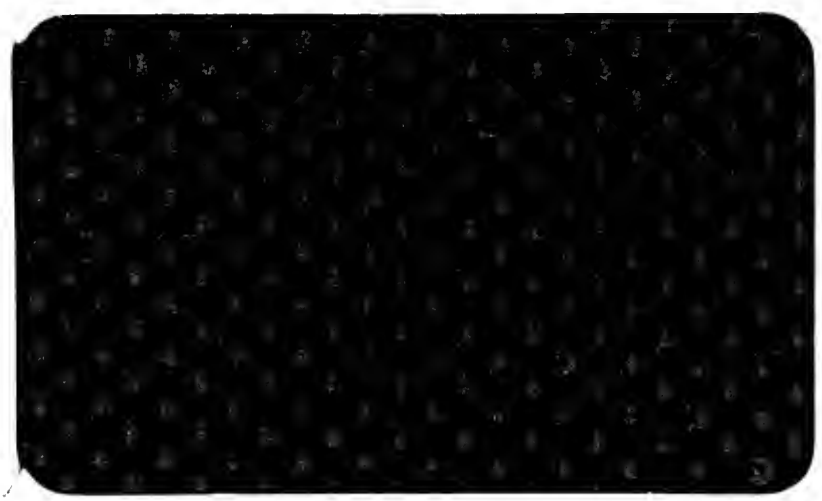

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Abstract

Monte Carlo studies have been carried out for systems of hard spheres in one (hard rods), two (disks) and three dimensions. The experiments are described in some detail along with the results. The existence of a phase transition in both two and three dimensions has been confirmed. In an attempt to study the transition further, the effect of imposing a gravitational field on the system was investigated and it was found that the field does not separate out the two phases. A possible model for what happens at the phase transition is suggested and discussed.

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Monte Carlo Studies of Systems of Hard Spheres

1. Introduction

Monte Carlo calculations for finding the equation of state and for investigating other properties of simple systems were first carried out by Metropolis[1] and his co-workers[2] at Los Alamos in the early nineteen-fifties. Since that time Wood and others[3-7] have continued these studies. Similar work has been done at Livermore by Alder and Wainwright[8-11] but they do exact dynamical, rather than Monte Carlo, calculations. In addition some work has been reported by Smith and Lea.[12] The large measure of success achieved by both the Los Alamos and Livermore groups encouraged us to try to extend these investigations. Because the Monte Carlo method seemed simpler (and we had some experience with it) we decided to use it. Experiments have been carried out with the hard core potential in one, two, and three dimensions, the one dimension case (hard rods) having been used only as a check on the method. It was already known from the earlier work that a phase transition exists in both two (hard disks) and three (hard spheres) dimensions and an attempt has been made to separate out the two phases by imposing a weak gravitational field onto the systems. In all cases periodic boundary conditions were used, except for a few runs in one dimension where reflecting boundaries were employed.

In the next section, a general description of the code is given. Sections 3,4, and 5 describe the work done in one, two, and three dimensions respectively. In section 6 some further results are discussed with particular emphasis on what seems to be happening at the transition and evidence for what is called "clumping" is presented. The effect of the gravitational field is described in section 7 and in the last section the results of these studies are summarized and plans for future work are outlined.

2. Code Description

In this section a detailed description of the code is presented. The three dimension case will be described but the methods used are the same in one and two dimensions and minor differences will be mentioned in the following sections dealing with the specific results for hard rods and disks. It should be emphasized at the beginning of this section that the procedures herein described are similar to those used by the early workers[1,2] and are discussed here because no full description of their work is readily available and the details were developed independently. Metropolis et al[1] give a proof that the procedure is ergodic and that the system approaches a canonical distribution. The proofs are not repeated here. However, the properties of the systems we are investigating are

in fact properties of the canonical distribution and hence the rate at which equilibrium is reached is a very important consideration. Generally, equilibrium is reached rapidly but in some cases, and these tend to be the more interesting ones, the approach to equilibrium in slow and much computation is needed to get meaningful results. Details will be given below in the discussion of the particular cases.

Most of the coding for this work has been done in IBM-7090/4 machine code (FAP) rather than in FØRTRAN. There are three very considerable advantages in using FAP. FØRTRAN was designed to carry out arithmetic calculations and translates arithmetic statements very efficiently. In executing logical statements, however, FØRTRAN is much less efficient and since the code does consist very largely of logical decisions coding directly in FAP is highly desirable. Some of the important details of the coding will be given but readers unfamiliar with the machine language can omit these portions. The second advantage of FAP is that it permits the use of full length (35 bit) fixed word arithmetic, an elementary feature of the machine but one not available with FORTRAN II. This arithmetic makes it possible to satisfy the periodic boundary conditions almost trivially and details are given below in the description of the particle motions. Finally FAP permits packing of information within a single machine word thus effecting a much needed saving of core storage.

The code consists of three parts viz. (i) initialization, (ii) random motions of the particles and (iii) taking appropriate statistics. The primary quantity evaluated is the radial (two-body) distribution function, $g(r)$, which is defined as the number of particles lying in a shell with inner radius r and outer radius $r + dr$, where r is measured from a given particle, all interparticle distances being measured from center to center. Since we are dealing with hard spheres, the minimum value of r is the sphere diameter, d_o, and $g(r) = 0$ for $r < d_o$. Actually $g(r)$ is found only for $d_o < r < Kd_o$ where K is a parameter which is chosen for each individual case. The most usual choice for K was 1.5 but values as high as 5.0 and as low as 1.0019 were used under certain special circumstances. Reasons for these choices will be discussed later.

(i) Initialization

The initialization procedure consists of two sections. In the first particle coordinates are obtained. In all cases the space used is the unit cell, the unit line in one dimension, the unit square in the plane and the unit cube in ordinary space, and as already stated periodic boundary conditions are imposed in all but a few cases. The hard core potential requires that no two particles overlap and a set of particle coordinates to satisfy this requirement could be found in an

infinite number of ways. In our codes the particles are started by placing them in a regular lattice arrangement, a choice made only in the interests of simplicity. Thus they are placed at regular intervals along the line in one dimension, in a regular hexagonal (trigonal) lattice in two dimensions and in a face centered cubic lattice in three dimensions. It is not always a trivial matter to realize these lattices so as to satisfy the periodic boundary condition properly in the plane and in ordinary space and the actual methods used are given in sections 3 and 4.

Once the particle coordinates have been obtained, the second part of the initialization procedure is carried out. This consists in finding, for each particle, a list called the NLIST of its neighbours, a neighbour being another particle lying within the sphere of radius Kd_o about the given particle. Thus the NLIST is a two-dimensional array consisting of a neighbour list for each particle. It is symmetric in that if A is a neighbour of B, that is A is a member of the NLIST of B, then B is a neighbour of A. However, to save storage by keeping just half the NLIST would vitiate its purpose which is to enable us to identify neighbours quickly. The particles are numbered and the beginning of a given NLIST is found by computing an address having been given the particle number. The end of each NLIST is signalled by a word of all zeros. The NLIST is found by examining every particle and inserting in the list those lying within the sphere defining the neighbourhood.

This procedure means that every pair of particles must be examined twice, once for A's NLIST and once for B's but this need be done only at the beginning of each run and at most takes a few seconds of computation.

Actually finding the members of the NLIST is simple enough except in cases where the neighbours lie on opposite sides of the box so that the image of one of them in the next cell is within the neighbourhood of the other. Here the FAP code is very efficient. The interparticle distance $X_{AB} = |X_A - X_B|$ is formed and compared with Kd_o. If $X_{AB} < Kd_o$ then A and B are neighbours. Of course in two (and three) dimensions the test must be made for the y (and z) coordinates too. If $X_{AB} > Kd_o$, it is possible that the image of particle A, say, in the adjoining cell is such that $X_{A'B} = |X_{A'} - X_B| < Kd_o$ where $X_{A'}$ is the coordinate of the image, that is $X_{A'} = X_A \pm 1$ where the positive sign is used for $X_A < \frac{1}{2}$, the negative sign otherwise (see Figure 1). In practice this second test is carried out differently, and X_{AB} is compared with $1-Kd_o$. If $X_{AB} < 1 - Kd_o$, the interparticle distance is taken to be $1 - X_{AB}$ which is the same as $X_{A'B}$. The actual coding for both tests follows. It is assumed that X_{AB} has been formed in the accumulator.

Figure 1

LAS	KD	Compare X_{AB} with Kd_o.
LAS	MKD	$X_{AB} > Kd_o$. Compare X_{AB} with $1-Kd_o$.
CØM		Complement, equivalent to subtracting 1.
TRA		$X_{AB} < Kd_o$. A,B are neighbours.
TRA		$X_{AB} < 1-Kd_o$. A,B not neighbours.

The annotation is not quite complete, in particular the fourth line (first transfer instruction) will be reached also if $X_{AB} > 1-Kd_o$ in which case A and B are neighbours too. Further the case of equalities has been ignored and could lead to serious trouble. In practice an exact equality is extremely unlikely but nonetheless it is explicitly excluded, except in the one-dimensional case, by requiring that

$$r_{AB} = \sqrt{X_{AB}^2 + Y_{AB}^2 + Z_{AB}^2} < Kd_o ,$$

a test which is made after the individual coordinates are examined. LAS is used instead of CAS since X_{AB} is formed as a signed number. In two and three dimensions the comment "A,B are neighbours" should read "A,B may be neighbours" since the test on Y_{AB}, Z_{AB} or r_{AB} may show that they are not neighbours. The individual coordinates are examined separately before r_{AB} is tested because in many cases it can be determined that two particles are <u>not</u> neighbours very quickly. Of course for those pairs which are neighbours this procedure is a bit

longer than necessary, but on the average considerable computing time is saved. The neighbour list is found by examining every pair of particles and inserting in the list those lying within the sphere of radius Kd_o.

In finding the NLIST, the interparticle distance r_{AB} is found and is recorded in the following way. The volume between $r_{AB} = d_o$ and $r_{AB} = Kd_o$ is divided up into 64 zones each of volume ΔV where

$$\Delta V = \frac{4}{3}\pi(K^3-1)d_o^3/64 \quad . \tag{1}$$

Each interparticle distance r_{AB} is then assigned a zone number m (m = 1,2,3.... 64) where m is chosen to satisfy the inequalities

$$(m-1)\ \Delta V + \frac{4}{3}\pi d_o^3 < \frac{4}{3}\pi r_{AB}^3 \leq m\ \Delta V + \frac{4}{3}\pi d_o^3 \quad . \tag{2}$$

Readers familiar with the IBM-7094 might note that the neighbour number is stored in the decrement portion and the distance zone number m in the address portion of the NLIST. This description is for three dimensions, the appropriate zone definition in one and two dimensions is exactly similar using lengths and areas respectively.

This method for finding the NLIST has been described for the case where a new problem is being run and the particles are started off in the regular lattice arrangement. Since it

frequently happens that the effect of the starting distribution persists for a long time, it is necessary to terminate some runs before an equilibrium condition is reached and to continue the computation at some later time. At termination, the current particle coordinates are punched out on cards. To continue the run later, these cards are read back into the machine and in the initialization phase the generation of coordinates is omitted, and the NLIST is obtained directly from the coordinates by the procedure given above. Information is coded on the first data card to distinguish between a new problem and the continuation of an old one. This first data card also contains the number of particles, the density and the number of cycles to be processed.

(ii) Random Motions

The heart of the procedure consists in the random motion of the particles. The prescription for moving the particles is the same as that given by Metropolis et al[1], namely,

$$\begin{aligned} X &\longrightarrow X + \alpha\xi_1 \\ Y &\longrightarrow Y + \alpha\xi_2 \\ Z &\longrightarrow Z + \alpha\xi_3 \end{aligned} \qquad (3)$$

where X, Y, and Z are the particle coordinates and α is the maximum displacement allowed. The ξ_i are random numbers

in (-1,1). Thus after a move, a particle is equally likely to be anywhere in a cube of side 2α centered about its original position. (In some later work particles were moved so that they are equally likely to be anywhere in a sphere of radius α centered about the original positions.) The prescription for moving a particle given by eq.(3) must satisfy the periodic boundary conditions for the unit cell. To understand how this is done, consider a particle which has been moved so that it crosses the right boundary of the cell at the plane $x = 1$. In this case its x-coordinate is greater than 1 and it must be reinserted at the left side of the cell with a coordinate equal to the fraction by which its coordinate exceeds unity. To code this in FØRTRAN requires a test and a floating point subtraction. In FAP, the store instruction gives the fractional part, just what is needed. This is exactly the same code as is used in making a move when no boundary is crossed. Should a move take a particle past the left hand boundary, the coordinate becomes negative and in this case adding one to the coordinate places the particle in the correct position near the right hand boundary of the box. The boundary conditions are tested and satisfied by just three machine instructions:

```
        TPL     A 1     If coordinate > 0, transfer to A 1.
        ADD     ØNE     Coordinate negative.  Add one.
A 1     STØ     X       In either case, store coordinate in X.
```

This coding assumes that the new coordinate has been found (see above). For higher dimensions, the procedure is repeated in each dimension.

Now it is possible that in the new position the moved particle overlaps one of the other particles in the system. α is so chosen that the only neighbours that can be overlapped are those lying within a sphere of radius Kd_o, so that a check of the NLIST suffices to determine that the move did or did not cause overlap. In the former case the move is forbidden since the hard core potential admits of no overlap and the particle is returned to its original position, but this is still counted as a "move", statistics being taken from the original coordinates, as explained by Metropolis[1]. In the latter case we say that the move is allowed, the particle remains in its new position and its new neighbour list is found. In examining the NLIST to see if there is overlap it is of course necessary to check the case where neighbours are on opposite sides of the cell boundary. The method used is precisely the same as that already described for finding members of the NLIST in the initialization phase.

For allowed moves the new NLIST is generated in the same way that the NLIST was found initially, namely, by examining <u>every</u> particle to see if it lies within the sphere of radius Kd_o from the moved particle in its new position. While this method is both conceptually simple and easy to code, it has the disadvantage that the time taken per move depends upon N

the number particles in the system. And so another method for generating the new neighbour list was devised. If α is sufficiently small, all the new neighbours must be found in the list of the old neighbours plus the "second" neighbours, that is neighbours of the old neighbours. The combined list is termed the "stack" and in the procedure used, the old neighbours are first entered in the stack and the second neighbours are examined and those not already in the stack are added to it. When the stack is completed, its members are examined one by one and those lying in the neighbourhood are compiled to form the new neighbour list. A schematic flow chart of this procedure is given in Fig. 2. Although in this method the time taken per move is independent of N, this time is quite long. In the three dimensional case the time per move is approximately the same in the two procedures for 864 particles (the maximum used). In two dimensions, where there are fewer neighbours, the use of second neighbours effects a considerable saving for large systems. For 22^4 particles it takes about the same time to search all the particles for the new neighbour list as to set up the stack and then scan it. The code is capable of handling up to 2016 particles which can be processed at the same time per move as a system an order of magnitude smaller. In finding the new neighbour list by either method, the distances between particle centers are calculated and recorded according to the zone number m, m being obtained as

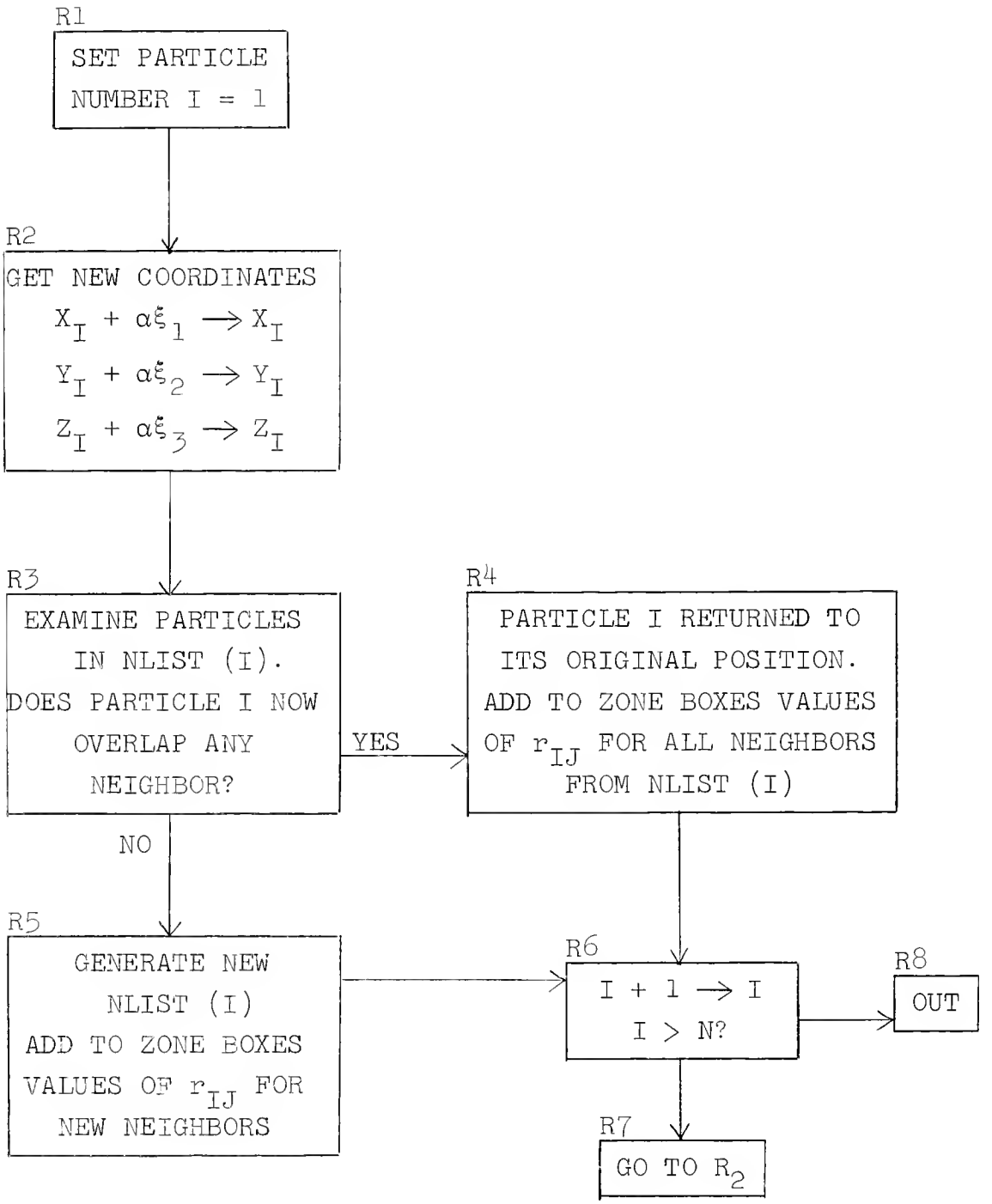

FIGURE 2. Schematic Flow Diagram for Making Random Moves.

described above in the initialization procedure.

When particle A is moved its NLIST is obtained as just described. The NLIST of all the neighbours of A must then be updated to correspond to the new situation. It is clear that if A is moved there are three choices for particle B, namely, (i) B is a neighbour before and after the move, (ii) B is an old neighbour but not a new one, and (iii) B is a new neighbour but not an old one. (The case where B is neither an old or new neighbour is of no interest.) In each case the list of B's neighbours must be brought up to date after the move. In the first case since A is already a member of B's neighbour list, only the distance r_{AB} expressed as a zone number need be altered and B's NLIST is searched until A is found and the new distance inserted in the address portion. If B is an old but not a new neighbour, A must be deleted entirely from B's neighbour list. And finally if B is a new but not an old neighbour, A must be inserted into B's NLIST. The neighbour lists are stored in numerical order as this greatly facilitates the searching procedure when either insertions or deletions must be made. The procedure used is to generate the new neighbour list of A without destroying the old NLIST and to compare entries in the old and new lists. Since both lists are in numerical order, it is simple to see if the members of the new list are also members of the old one, and if not to make the appropriate insertion or deletion

depending upon whether the new list neighbour number is less than or greater than the current old list neighbour number being examined . When a neighbour appears in both lists, then only the interparticle distance zone number has to be adjusted. If the lists were not arranged in numerical order the search to find the common members and to determine the necessary insertions and deletions would be very complicated. All lists are generated in numerical order so this order is maintained by making insertions in the correct places. It should be noted that after a deletion the list is closed up for otherwise the size of the lists (with blanks) could grow without limit. Maintenance of the order requires moving many members of the list up or down depending upon whether there has been an insertion or a deletion, and this is often very time consuming. However, no suggestion for eliminating or speeding up these procedures has yet proved workable except in some special cases. For hard rods the particles cannot change their relative positions so the neighbour lists can be kept fixed and only the distances need be changed. And at high densities for both two and three dimensions the particles become fixed in their relative positions and the same situation obtains. We did not alter our codes to take advantage of these special situations because in these cases the equilibrium distribution is reached rapidly with the existing codes. It is of interest to note that a decade ago when machines were much slower Rosenbluth[2] did find it advantageous to speed up his codes

in this way.

In two dimensions the NLIST can hold up to nine members for 2016 particles and since the end of each individual NLIST is signalled by a blank word (all zeros) the total size of the array is 20160. In three dimensions the NLIST can hold up to 23 members for 864 particles. The number of closest neighbours at close packing is 6 and 12 in two and three dimensions respectively; thus the size of the NLIST puts a rather severe limitation on K, so that $K \lesssim 2$. For low densities where there are fewer neighbours K could be increased somewhat. Clearly the size of the NLIST is limited by the size of the memory of the IBM-7094 which is 32768 words. If we desired $g(r)$ for $r > 2d_o$ we might amend the code by permitting fewer particles and enlarging the size of the NLIST per particle, or else maintain the NLIST for near neighbours and compute the interparticle distances r_{AB} for all pairs at each move, a very time consuming procedure. Fortunately the interesting region is for r small and we usually set $K = 1.5$.

The validity of the method does not depend in any way upon the order in which the particles are moved so long as any possible configuration can be reached in a finite number of moves. The two obvious ways of ordering the moves are serially and randomly. We have chosen the former because it is simpler to code and because it facilitated debugging. If we detect an error and know which particle was moved last we know also which

particles have been moved previously, information which would be difficult to obtain if the particles to be moved were chosen at random. In this discussion we have used the word "move" to include those cases where the move is forbidden and the particle is returned to its original position.

(iii) Statistics.

So far the only statistic mentioned was the interparticle distance r_{AB} or to be more precise the zone number m corresponding to r_{AB}. At each move all the interparticle distances pertaining to the moved particle are tallied. The distribution of these tallies after many moves properly normalized is the two body radial distribution function $g(r)$. The reader is again reminded (see Metropolis et al[1]) that this tally must be made even if the actual move is forbidden, and in this case the tallies are taken directly from the NLIST for this particle. Once $g(r)$ is known the pressure is computed from the equation[13]

$$\frac{pV}{NkT} = 1 - \frac{2\pi N}{3VkT} \int_0^\infty g(r) \frac{d\phi}{dr} r^3 dr \qquad (4)$$

where p is the pressure, V the volume, k Boltzmann's constant, T the temperature and ϕ the interparticle potential. For the square well,

$$\phi(r) = \infty \qquad r < d_o$$
$$\phi(r) = 0 \qquad r > d_o \ , \tag{5}$$

the integral is easily evaluated by making use of the fact that $e^{\beta\phi(r)}\, g(r)$ is continuous. $\beta = (kT)^{-1}$. Then we have for the integral in (4),

$$\int_o^\infty g(r)\, \frac{d\phi}{dr}\, r^3 dr = \int_o^\infty e^{\beta\phi(r)}\, g(r)\, \frac{d\phi}{dr}\, e^{-\beta\phi(r)}\, r^3 dr$$

$$= -\frac{1}{\beta} \int_o^\infty e^{\beta\phi(r)}\, g(r)\, \frac{de^{-\beta\phi(r)}}{dr}\, r^3 dr \ .$$

Now $\frac{d}{dr}\, e^{-\beta\phi(r)} = \delta(r-d_o)$ for the square well potential (Eq.(5)), so we get

$$\frac{pV}{NkT} = 1 + \frac{2\pi}{3V}\, N\, g(d_o)\, d_o^3 \tag{6}$$

where for convenience the integral is evaluated at $d_o + 0$. It was stated above that it is $g(r)$ which is obtained, but actually what is found is the number of particles B_m in each of the 64 zones and it is necessary to relate the B_m to the two-body distribution function. Since B_m is averaged over one cycle, that is N moves, we have

$$B_m = N\, \Delta V\, g(r_m) \tag{7}$$

where $g(r_m)$ is the value of the two body distribution function at the mid-point of the m^{th} zone. Thus we find the distribution function at the mid-point of each zone and to get the value at $r = d_o$ we must extrapolate to the beginning of the first zone. This is done by plotting the first few values of B_m and extrapolating one-half zone. An example of this extrapolation is shown in the next section. We denote the extrapolated value by $B_{\frac{1}{2}}$ and then have from Eq.(7)

$$B_{\frac{1}{2}} = N \Delta V \, g(d_o) \, . \tag{7'}$$

Substituting Eq.(7') into Eq.(6) and using for ΔV the expression given in Eq.(1) we have

$$\frac{pV}{NkT} = 1 + \frac{32 \, B_{\frac{1}{2}}}{V(K^3-1)} \, . \tag{8}$$

In one and two dimensions the corresponding equations are,

$$\frac{pL}{NkT} = 1 + \frac{32 \, B_{\frac{1}{2}}}{L(K-1)} \tag{9}$$

where L is the length of the box, and

$$\frac{pA}{NkT} = 1 + \frac{32 \, B_{\frac{1}{2}}}{A(K^2-1)} \tag{10}$$

where A is the area of the box.

After every cycle further statistics were recorded. The total number of neighbours inside the sphere of radius Kd_o is found by getting the sum $\sum_m B_m$. The nearest neighbour to each particle was found and a tally made of the distance to the nearest neighbour in terms of the zone number m. This is simply done by examining the NLIST of each particle for the smallest m. Also for each particle the average distance of all neighbours lying within the sphere of radius Kd_o was computed by adding up the zone numbers for all the neighbours recorded in the NLIST and dividing by the number of neighbours. In the division only the integral part of the quotient, unrounded, was found and these average distances were again tallied by zone number. Finally after an arbitrary number of cycles the migration distance of each particle was computed and a record kept of the distribution of these migration lengths. The results obtained and implications of these statistics will be discussed below.

In the next three sections the results of the Monte Carlo experiments in one, two, and three dimensions respectively are presented. Although several aspects are discussed, it is the equation of state which is the fundamental concern. The pressure is obtained by Eq.(8), (9) or (10) as appropriate and the volume is expressed as the ratio of the total volume available to the volume occupied by the particles at close packing. Thus this ratio is greater than unity and increases as the density

decreases. In one dimension the "volume" is simply L/L_o and equals d/d_o where d is the average interparticle spacing. In two dimensions, the "volume" $A/A_o = f\, d^2/d_o^2$ where f is a fitting factor which is close to unity (see § 4). In three dimensions $V/V_o = (d/d_o)^3$ where now d is the average spacing of nearest neighbours in the regular lattice. Further details are given in the descriptions which follow.

3. Hard Rods

In one dimension, the exact analytic solution for the radial distribution function for any number of hard rods in a periodic box is known.[14] Thus the Monte Carlo calculations were carried out as a check on the procedures and to test out the code. As an example of the results obtained, the graph of $g(r)$ for $N = 64$, $L/L_o = 1.492$ is shown in Figure 3. The Monte Carlo results are indicated by the crosses while the smooth curve is the analytic solution at the same density but for an infinite number of particles. Since the number of neighbours is so limited we can take a rather large value of K and the computation was made for $K = 5.0$. Similar good agreements between the Monte Carlo and analytic results were obtained for the equation of state. For $N = 64$ the largest value used, the system is virtually indistinguishable from a system with $N = \infty$ and agrees to within the statistical

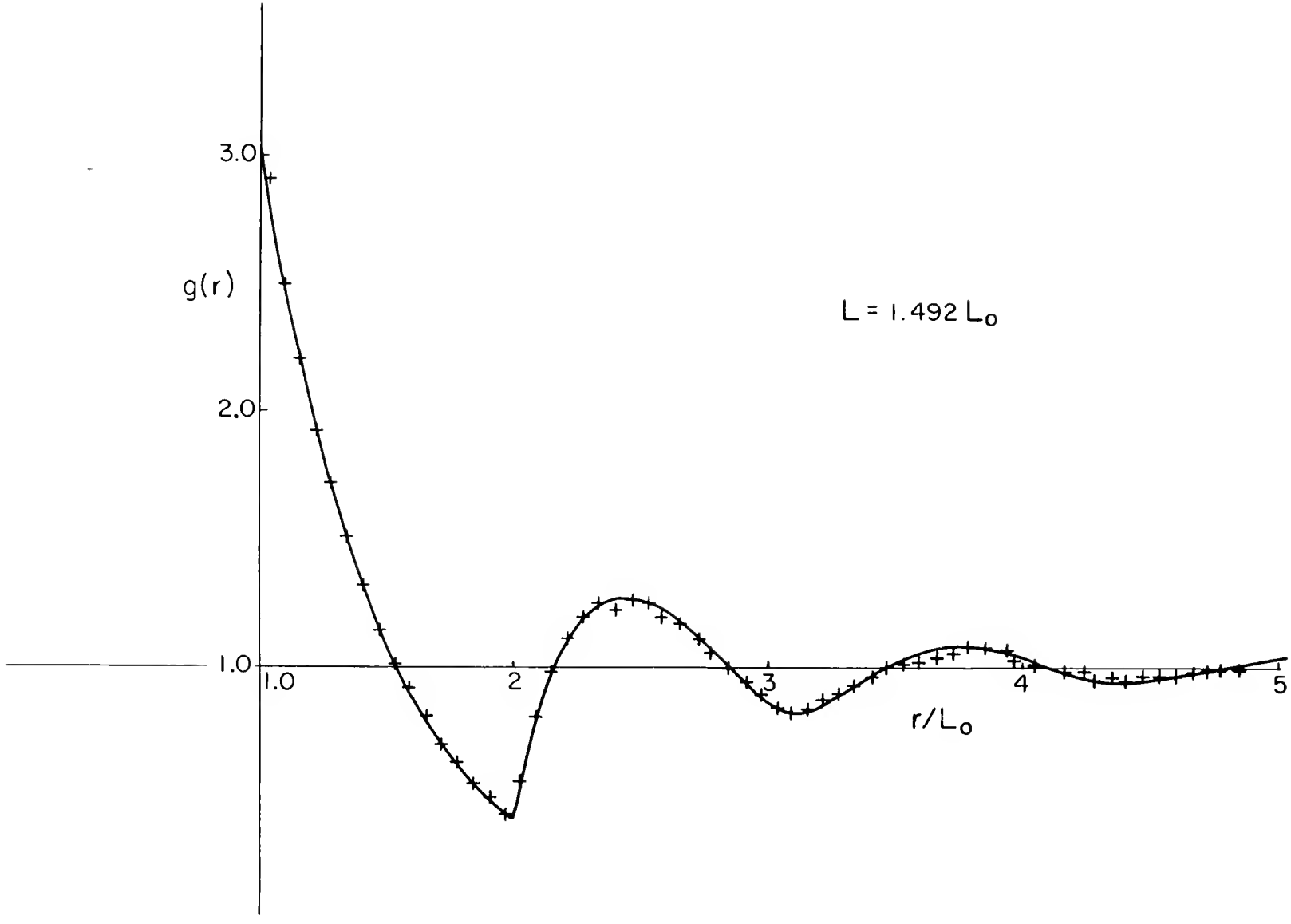

Figure 3. Radial Distribution Function for Hard Rods

fluctuations with the known equation of state[14], $pL/NkT = 1/(1-L_o/L)$. In Fig. 4 this equation of state is plotted along with some Monte Carlo results for N = 4, N = 16, and N = 64. The very close agreement in the latter case with the analytic solution gives an indication of the statistical errors which arise in the Monte Carlo procedure, since the difference between 64 particles and an infinite system is very small. Examination of Fig. 3 indicates what is involved in extrapolating the Monte Carlo results to determine $g(d_o)$. Since the code is so written that 64 zones are always used the distance to be extrapolated is greatly reduced by taking smaller values of K. For K = 1.5 the error in extrapolation will be less than the inherent statistical errors in the data.

A few runs were made with reflecting instead of periodic boundaries. Here, too, the analytic solution for the radial distribution function is known and the Monte Carlo computations gave results which were in very good agreement with the theory.

Kac, Uhlenbeck and Hemmer[15] have shown that a phase transition will take place in a system of hard rods to which a weak long range exponential attractive potential is added to the infinite repulsive core in the limit as the strength of the attractive potential goes to zero and its range to infinity. Of course it is not possible to realize the limiting situation with a Monte Carlo type code but the effect of a moderately weak, fairly long range potential can be examined. Because

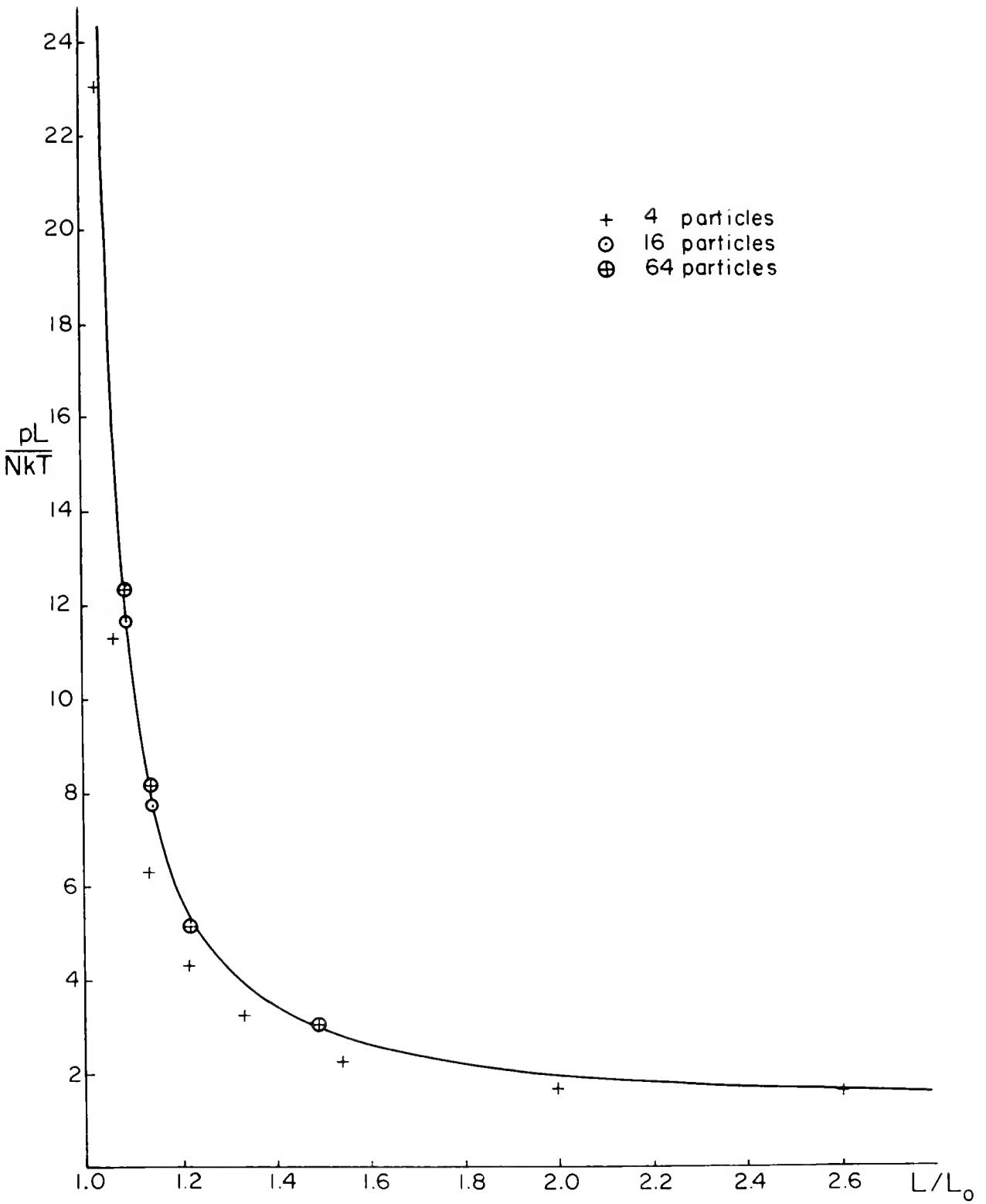

Figure 4. Equation of State for Hard Rods

the time required to compute exponentials is large, the attractive force was replaced by a linear potential of the form $\phi(x) = \gamma(x-k)$ for $d_o \leq x \leq k$; $\phi(x) = \infty$ for $x < d_o$ and $\phi(x) = 0$ for $x > k$. γ, the strength of the potential was left arbitrary and the range k was chosen so that $k = 5d_o$. Only a few runs were made and for the parameters chosen, the distribution functions were found to be only slightly altered from those obtained with the simple hard core potential. Part of the motivation for this calculation was to gain experience with interparticle forces containing an attractive tail and this particular choice was made in the hope of making some comparisons with the predictions of Kac and Uhlenbeck. It is clear, however, that the short range linear potential is much too crude an approximation to an exponential long range force and that much more work will have to be done to get meaningful results. On the other hand it is probably not too difficult to derive analytic results for $g(r)$ for a short range potential and such a derivation would be very useful for stimulating further Monte Carlo explorations.

4. Hard Disks

In two dimensions we used for the most part the same lattice arrangement described by Metropolis et al[1]. The disks are placed in a unit square box and the boundaries are periodic. The close packed hexagonal (trigonal) lattice can be viewed as having rows of touching disks with alternate rows displaced by the disk radius, r, with the distance between rows = $\sqrt{3}\ r/2$. Since this distance is an irrational number the close packing array cannot be realized exactly, but by choosing the ratio of the number of disks per row to the number of rows to be close to $\sqrt{3/2}$, the close packing array can be approximated. Following Metropolis, 224 particles were arranged in 16 rows of 14 disks each. At close packing the disks in each row are just touching (i.e. $2r = 1/14$) in the x-direction, and the hexagonal lattice will be realized when the rows are $\frac{\sqrt{3}}{2}\left(\frac{1}{14}\right)$ apart. Thus for 16 rows the total distance required in the y-direction is $f = \frac{16}{14} \cdot \frac{\sqrt{3}}{2} = \frac{.8660}{.8750} = .98974 < 1$, so this lattice will fit into the unit cell with a little space left over. We call f the fit of the lattice. The periodic boundary condition requires an even number of rows, but not necessarily an even number of disks in each row. This can be seen from Fig. 5. The disk at the origin has its image in the box at the right at (1,0) and in the box on top at (0,1). Alternate rows have their centers displaced by the disk radius as shown. If there were an odd number of rows, the last row at the top

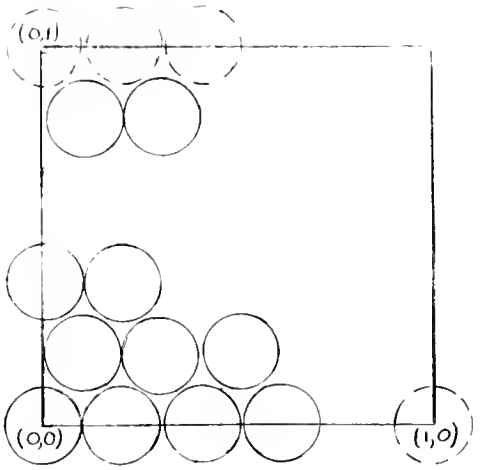

Figure 5. Hexagonal Lattice

of the box would not be so displaced from the row shown dotted in the figure which is the image of bottom row, and the disks would not fit without overlap at close packing. Thus a 15 by 13 lattice could not be used even though $\frac{13}{15}$ (=.8666) is very nearly equal to $\frac{\sqrt{3}}{2}$. However, by doubling the number of rows and the number of disks per row a 30 by 26 lattice is obtained with the same fit, and this lattice was used in a few cases. The reason for requiring a good fit to the periodic cell at close packing is discussed below. Wood[7] has solved this problem of fitting by using a rectangular box and in this way any number of particles in any even number of rows can be used. Initially the disks are arranged in the hexagonal array with diameters d_o to give the desired density in the box. The NLIST is then obtained as previously explained and the particles are moved one at a time as already described. Several cycles (a cycle is defined as N moves, each disk moved once) are processed without recording statistics in order to destroy the original regular arrangement. The number of cycles needed to effect this randomization depends upon both the density and on N. As explained above, the coordinates are punched out on cards

after every run so that if more statistics are desired either because the system is not randomized or because the fluctuations are too large the run can be continued. The cards punched out after a run can be used to give initial coordinates for a new run at a lower density; the disk diameters are simply made smaller. However, they cannot be used for a higher density since with larger disks there will be some overlapping.

The criterion that an equilibrium state has been reached is somewhat subjective. To aid in evaluating the results, the radial distribution function $g(r)$ is printed out periodically during the run. There is no difficulty in deciding that equilibrium has been reached when $g(r)$ shows no changes except for the statistical fluctuations inherent in the Monte Carlo method. If $g(r)$ is changing because of the influence of the starting distribution, the run is continued until an apparent equilibrium state is reached. The question of metastable states and the related problem of accessibility of states has not been explored except in the neighbourhood of the transition where there seem to be two states. However, it is only at high densities where the disks cannot move freely that metastable states could exist. The fact that very extensive calculations have shown no evidence of metastable states is no indication for or against their existence because we always start off from the same regular hexagonal lattice and so may always be excluding certain states from the

beginning. To check this matter further we would have to begin from a throughly randomized state at low density and increase the density in some adiabatic way but because of the resulting overlap this cannot be done with our code. It should be possible to devise a method whereby the overlapped particles will be moved slightly and the overlap removed. Wood[7] has a discussion on accessible states to which the interested reader is referred.

Using the Los Alamos MANIAC computer, Metropolis et al[1] were able to obtain a point on the equation of state curve in four or five hours of computing time and this represented sixty-four cycles of moves. In this early work no indication of a phase transition was found. In fact the first clear evidence for a phase transition in two dimensions was not published until 1962 by Alder and Wainwright[16] whose calculations were dynamical. At about the same time Wood[7] published some results he obtained using the Monte Carlo method. However, it was early realized that Metropolis had not been able to continue his chains long enough and the only reason why the transition was not reported earlier is that efforts[2-5] were concentrated on examining the situation in three dimensions where the transition is more marked. In figure 6 the equation of state is plotted for the 224 particle system and shows the phase transition at $A/A_o \approx 1.31$. Also plotted in Figure 7 is the number of neighbours inside the sphere of radius $1.5d_o$ and

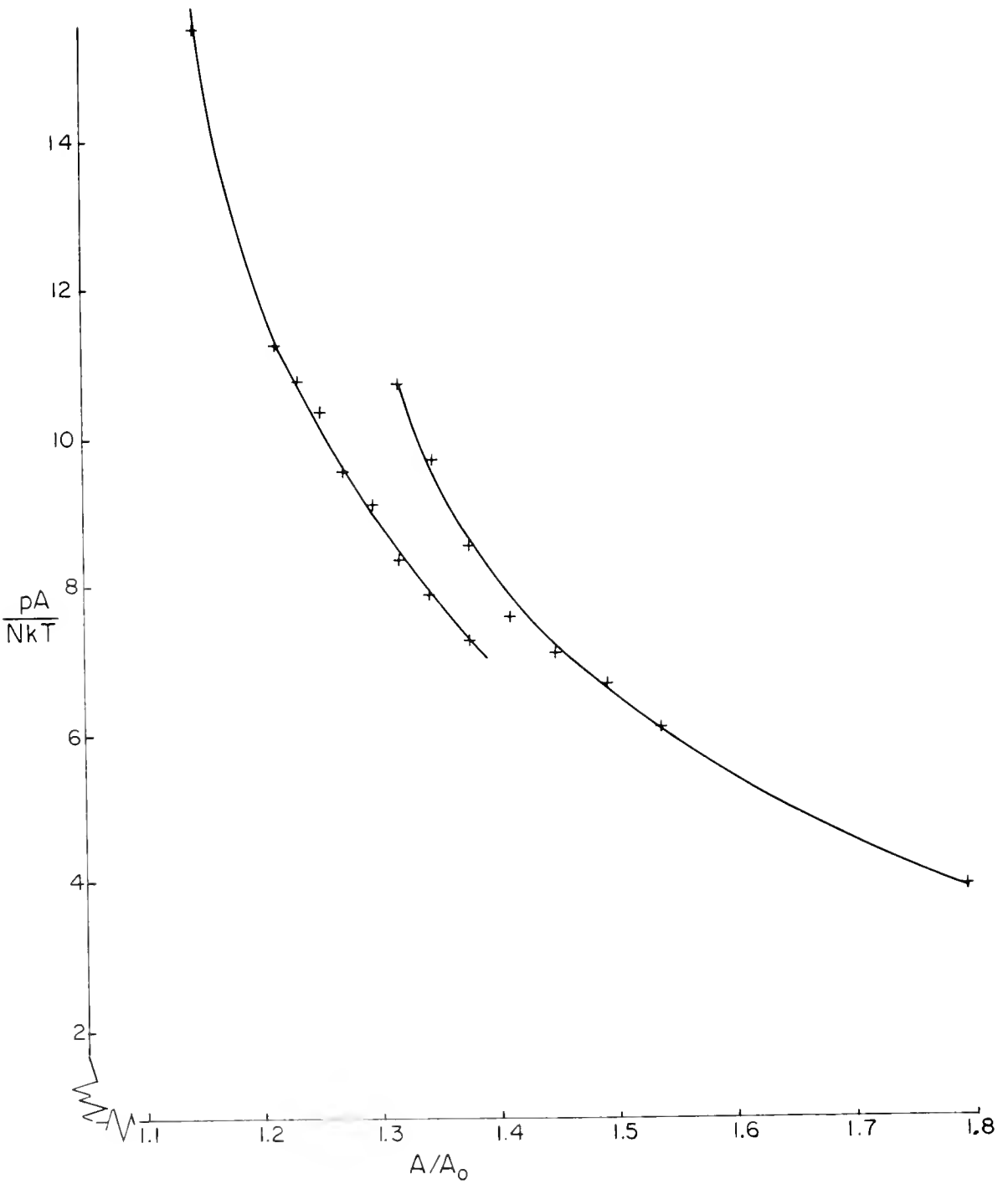

Figure 6. Equation of State for Hard Disks (224)

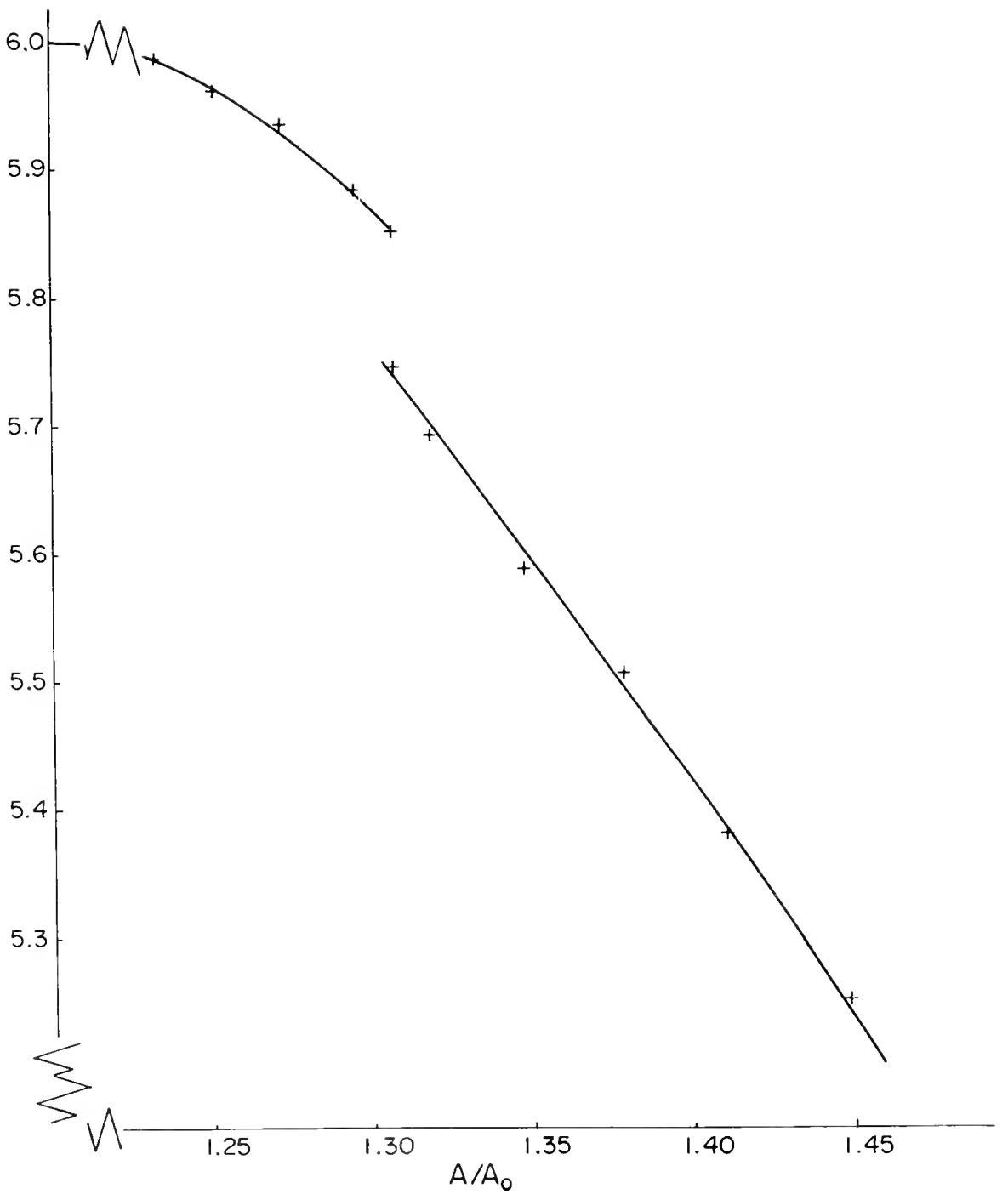

Figure 7. Average Number of Neighbours Out tc $1.5d_0$

this shows a discontinuity at the transition. Most of our work was done with 224 disks in the 16 by 14 array but some runs were made with 9(3x3), 12(4x3), 56(8x7), 223(16x14 with one particle omitted), 225(15x15), 780(30x26), and 2016(48x42) disks. No extensive work has been done to compare results with these different lattices, but at low densities all these systems give the same pressure-volume relationship.

At high densities, near close packing, the way the disks fit in the box becomes important. This is most easily seen in the 3x3 case where particles tend to arrange themselves in a rectangular, rather than a hexagonal pattern in order to satisfy the periodic boundary conditions. This puts the particles closer together and so gives a higher pressure than in the 16x14 lattice where near hexagonal packing can be realized. For 12 disks in 4x3 array in a square box the particles cannot be very closely packed in the sense that a hexagonal lattice does not fill up the box. A discussion of the packing problem is given in Salsburg and Wood[17]. These authors also derive an expression for the equation of state at very high densities on the basis of free-volume theory. In Table I the pressures obtained by Monte Carlo and by the free-volume theory are compared. In the first part of the table results are given for 16x24(224) and 48x42(2016) lattices for both of which the fit is .98974. In the second part results for the 30x26 (780 disks) lattice are given. Here the fit is .99926. It is seen that Monte

	$\frac{A}{A_o}$	pA/NkT	
		Monte Carlo	Free Volume
(a)	1.0766	29.1	27.0
	1.0427	51.9	47.6
	1.0287	79.8	70.3
	1.0183	154.3	110.2
	1.0123	499	163.2
(b)	1.0047	443	429
	1.0027	796	741
	1.00123	2489	1628
	1.00098	4169	2027

TABLE I. Comparison of Monte Carlo Calculation of Pressure with Free Volume Theory. In part (a) the fit is .98974 (224 or 2016 particles); in part (b) it is .99926 (780 particles).

Carlo pressures begin to depart from free-volume theory at densities such that $(A/A_o)^{-1}$ is about equal to the fitting factor f, and this is about what one would expect. Thus the data in Table I indicate that at very high densities the Monte Carlo results would agree with free-volume theory for an arrangement of particles which exactly fits the available area at close packing.

At low densities we expect the Monte Carlo computations to agree with the first few terms in the virial expansion. We have for the latter[1]

$$\frac{pA}{NkT} = 1 + \frac{\pi}{\sqrt{3}} \frac{A}{A_o} + 2.5727 \left(\frac{A}{A_o}\right)^2 + 3.179 \left(\frac{A}{A_o}\right)^3 + \ldots \quad . \quad (11)$$

In Table II we summarize some results obtained. The agreement shown is well within the accuracy of the Monte Carlo calculations.

N	$\frac{A}{A_o}$	PA/NkT	
		Monte Carlo	Virial
225	4.62	1.533	1.545
224	4.69	1.555	1.525
225	13.44	1.137	1.149

TABLE II. Pressure at low density

The very good agreement obtained between our results and theoretical predictions at both high and low densities gives good evidence that the code is working properly and in fact these predictions were used as a check on the code during debugging.

Until the existence of a phase transition was clearly established by the early Monte Carlo work and by the dynamical calculations of Alder and Wainwright, it was believed that such a transition was associated with long range intermolecular forces and so could not exist in a system of hard spheres. It was further argued that a first order phase transition has a latent heat and that without a temperature no latent heat could be present[18]. However, Fisher[19] points out that the latent heat can be a purely entropic effect and thus a first order transition is not ruled out. The nature of the phase transition is discussed further in sections 6 and 7.

One of the characteristics of systems of hard spheres and hard disks that has been reported is that in the transition region the system jumps from one branch of the equation of state to the other and back again. In every case the system is started off in the regular lattice arrangement and this means that the system begins on the high density or solid branch of the equation of state. We have made some long runs of several thousand cycles with 224 disks and have seen no evidence of a jump other than the one near the beginning when the system does undergo a

transition from the high density (solid) branch to the low density (fluid) one. A typical case is shown in Figure 8 which gives the values of $B_{\frac{1}{2}}$ for 200 intervals of 50 cycles each, 10000 cycles in all at $A/A_o = 1.3197$. $B_{\frac{1}{2}}$ of course is related directly to the pressure as shown above in Eq. (10). It is seen that $B_{\frac{1}{2}}$ starts at a relatively low value. This corresponds to the solid branch of the equation of state and the pressure obtained by taking an average value of $B_{\frac{1}{2}}$ over the first few intervals is exactly what one gets by extrapolating the equation of state from higher densities. After several groups of 50 cycles, the values of $B_{\frac{1}{2}}$ increase and fluctuate about the higher value from then on. We interpret these high values of $B_{\frac{1}{2}}$ (and so the pressure) as indicating that many of the particles have clumped together leaving a few disks relatively free to move. And an examination of the neighbour lists shows that it is at the transition that disks are first able to move out of their original neighbourhoods. Other workers have reported jumps from one phase to the other and back again. In particular Wood[7] reports no such jumps in a system of 12 disks but does describe the "jumpy" mode for 48. In no case have we observed any jump other than the one described where a system started off in a regular lattice arrangement undergoes a transition from the solid to fluid branch of the equation of state.

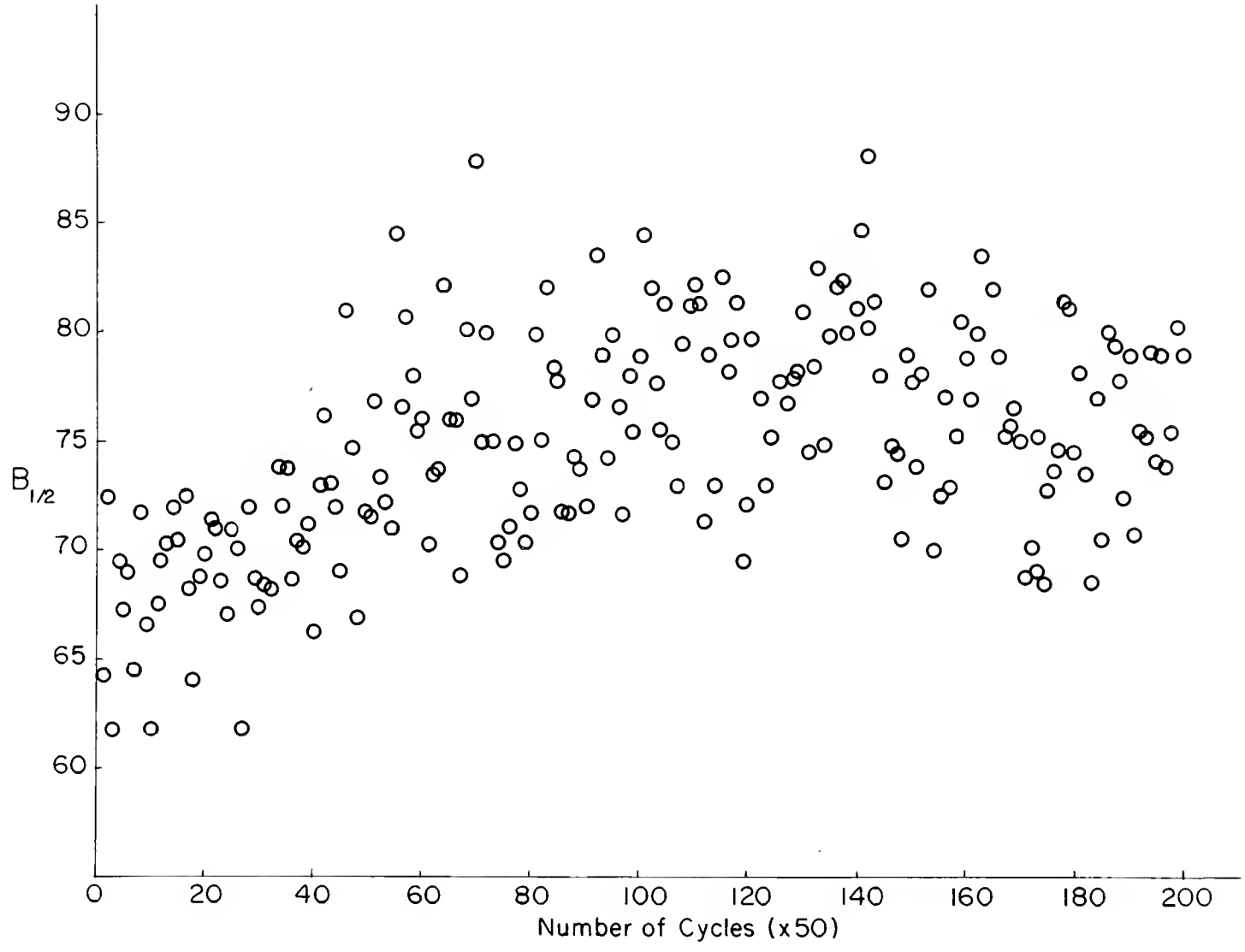

Figure 8. Variation of $B_{1/2}$. $A/A_0 = 1.3197$. Each point represents average over 50 cycles.

5. Hard Spheres

The extension from two to three dimensions is quite straightforward. The problem of fitting hard discs into a square box has been discussed and one might think that fitting spheres into a cube would be even more difficult. Fortunately this is not the case since under certain circumstances spheres will fit exactly into the unit cube. It is well known that there are two close packing arrangements for spheres, namely, the face centered cubic and the regular hexagonal lattices. Starting from the two dimensional hexagonal lattice the former can be viewed as having sets of three layers each one displaced from the one below it, while the latter consists of sets of just two layers. Only the face centered lattice is used in our work and in setting up this lattice it is easier to think in terms of the face centered cube and ignore the relationship to the two dimensional lattice. For values of N given by $N = 4j^3$ where j is any integer the spheres fit exactly into a unit cube so there is no fitting problem in three dimensions. Experiments have been run with $j = 2,3,4$ and 6 corresponding to $N = 32$, 108, 256 and 864 particles. To set up the face centered lattice, the first sphere is given coordinates (0,0,0) and then the next $j-1$ spheres are given coordinates $(i,0,0)$ where $i = \frac{1}{j}, \frac{2}{j}, \frac{3}{j}, \ldots\ldots \frac{j-1}{j}$. The next row in the $z = 0$ plane consists of j particles with y- coordinate $\frac{1}{2j}$ and x coordinates $\frac{1}{2j}, \frac{3}{2j}, \frac{5}{2j}, \ldots\ldots \frac{2j-1}{2j}$. As with the disks,

the third row begins at $x = 0$ again moved $\frac{1}{2j}$ in the y direction. In this manner $2j$ rows are set up in the y direction filling up the z=0 plane. Then $2j-1$ planes are set up in the z direction at intervals of $\frac{1}{2j}$ so z is treated exactly as was y. Thus at close packing the nearest neighbour distance $d = \frac{\sqrt{2}}{2j}$ corresponding to the fact that nearest neighbours in a face centered lattice are not at the corners of the cube, but from the center of the face to the corner. As already noted volume is measured as the ratio $\left(\frac{V}{V_o}\right) = \left(\frac{d}{d_o}\right)^3$ where d_o is the sphere diameter. Many authors use instead a quantity η defined by $\eta = \frac{\pi\sqrt{2}}{6}\frac{V_o}{V}$. Thus $\eta = .74048$ when $V/V_o = 1$ and decreases with decreasing density. η is the volume occupied by the spheres so that $\eta = 1$ means that the space is completely filled, that is with cubes.

No attempt has been made to work with the regular hexagonal lattice. It is known to have the same density as the face centered lattice and we expect that it will give the same results for the radial distribution function except possibly at very high densities. At close packing the radial distribution of the two lattices are not the same but our concern is whether they give the same equation of state. This question is closely related to the problem of accessibility of states mentioned above.

The first Monte Carlo calculation of properties of rigid spheres was made by Rosenbluth and Rosenbluth[2] who obtained

radial distribution functions for many densities and also a graph of the equation of state. At very high densities they found that the maximum value for $g(r)$ does not occur at the sphere diameter d_o but at a slightly larger value of r. They state that the pressure found from the Monte Carlo calculations is less than that given by the free volume equation of state, ascribing this result to the lowering of the pressure due to the decrease of $g(r)$ and hence of the molecular density at $r = d_o$. We have carried out extensive calculations in the region $V/V_o \lesssim 1.03$ and our results are summarized in Table III.

$\frac{V}{V_o} - 1$	PV/NkT	
	Monte Carlo	Free Volume
.03157	98.7	95.2
.02555	106.6	108.3
.01181	252.3	254.8
.00588	517.	509.
.00293	999.	1020.

TABLE III. Equations of State at High Densities

The Monte Carlo results are compared with the free-volume theory of Salsburg and Wood[17] which neglect corrections of $O(1)$. All values given in Table III are for systems of 864

spheres. Since the Monte Carlo results quoted are subject to the usual statistical fluctuations as well as to inaccuracies in extrapolating $g(r)$ to $r = d_o$ the agreement shown must be considered very good. It should be strongly emphasized that in obtaining the value of the radial distribution function at contact the curve is extrapolated downwards as shown in Fig. 9 where a part of the curve of $g(r)$ is plotted for the case $V/V_o = 1.002935$. From the figure the reader can readily see what is involved in the extrapolation. At these high densities $g(r)$ consists of a number of sharp peaks and since only the region near $r = d_o$ is of interest K-1 is taken to be very small, 0.0078125 in the case plotted. Better accuracy could be obtained in two ways. The extrapolation error can be reduced by reducing the zone size either by reducing K or increasing the number of zones. It is difficult to do the latter since the code is arbitrarily limited to 64 zones and K can be reduced only at very high densities since there is a relationship which must be preserved between K and α, the maximum move. The second way of improving the accuracy is by averaging over more moves; for results given in Table III the average is taken over 100 cycles after an initial run of 110 cycles to eliminate any effect of the starting lattice.

The peaking of the radial distribution function $g(r)$ slightly away from $r = d_o$ is likely an indication of a crystalization of the system. The peaking does not occur,

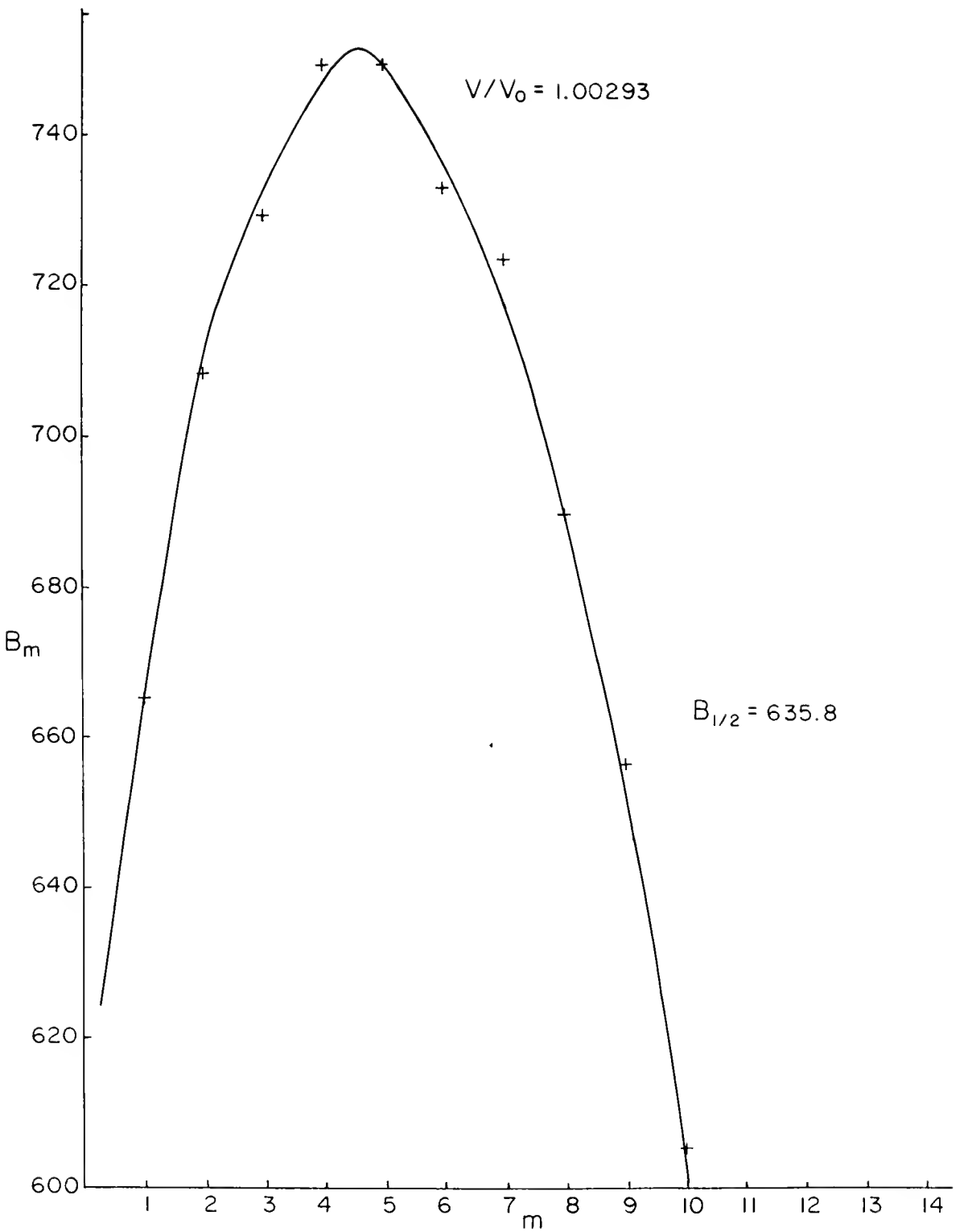

Figure 9. Radial Distribution Function at a High Density. Hard Disks.

however, at the average interparticle spacing d but at about one-half the distance between d and d_o. In Table IV results are given for d_M the distance at which $g(r)$ has its maximum. d_M is obtained from the plot of $g(r)$ as in Fig. 9 and as can be seen from this figure it is difficult to get d_M exactly. What is interesting about the values of d_M though is that they show no tendency to converge either to d_o or to d.

V/V_o	d/d_o	d_M/d_o
1.04194	1.01379	1.0077
1.02555	1.00844	1.0062
1.01181	1.00392	1.0020
1.00588	1.00196	1.0011
1.00293	1.00098	1.0005

TABLE IV. Peaking of $g(r)$ at d_M

Comparisons were also made with Wetheim's[20] solution of the Percus-Yevick equation but his values are up to an order of magnitude smaller at the highest densities considered than the values given in Table III. This is not surprising since the Percus-Yevick solution gives negative values for $g(r)$ at high densities and so could not be expected to be even approximately correct.

As regards the phase transition, Rosenbluth and Rosenbluth[2] find that it "occurs fairly gradually" so that they are unable to determine whether a phase transition occurs or not. Later calculations[4,8,11] made in the region of the phase transition show a sharp discontinuity in the equation of state. We have confirmed these observations and as in the case with disks have carried out several long runs to see if the system had any tendency to "jump" from one phase to the other. In one typical case with 864 spheres, the system was started in the regular face centered lattice with $V/V_o = 1.5155$. The system remained in the solid phase for about 1000 cycles and then rather gradually jumped to the fluid phase over the next 2500 cycles. The system was followed through 8000 more cycles but showed no tendency whatsoever to revert to the solid phase. At lower densities, that is higher values of V/V_o the jump to the fluid phase occurs after fewer cycles and is much less gradual. For example, at $V/V_o = 1.5396$, the system is in the fluid phase after 2000 cycles and at $V/V_o = 1.5496$ after only 400 cycles. At still lower densities the system is found to be in the fluid phase right from the beginning. For higher densities ($V/V_o \lesssim 1.50$) the system never undergoes a transition, in particular 5600 cycles were run for $V/V_o = 1.493$ and no tendency to undergo a transition was observed.

It may be argued that the jump from one phase to the other is a cooperative phenomenon and therefore is much less likely

with a large number of spheres (864) than for a smaller number. That there is some truth in this is attested by the fact that for smaller systems (32,108,256) the jumps from the initial solid phase to the fluid do occur after fewer cycles and tend to be less gradual. It should be noted too that the density at which the transition occurs varies slightly with N, increasing as N increases. This point is discussed further in the next section. Also no tendency to revert from the fluid to the solid was observed even for the smallest system.

In Fig. 10 the equations of state for 32 and 864 particles are plotted. These graphs are essentially the same as the one given by Wood, Parker, and Jacobson[5] but do exhibit the differences as N varies. In Fig. 11 the average number of neighbours out to $1.5\ d_o$ is plotted as a function of volume for 864 particles, and here, as in the case of disks, the discontinuity at the transition is clearly evident.

At low densities the virial expansion[2,13] gives

$$\frac{pV}{NkT} = 1 + 4\eta + 10\eta^2 + .18.11\eta^3 + \cdots . \qquad (12)$$

For $\eta = .0926$ this gives 1.470 and the Monte Carlo 1.463 and at $\eta = .0571$ the values are 1.260 and 1.263 respectively. This agreement is excellent in view of the uncertainity of the Monte Carlo calculations.

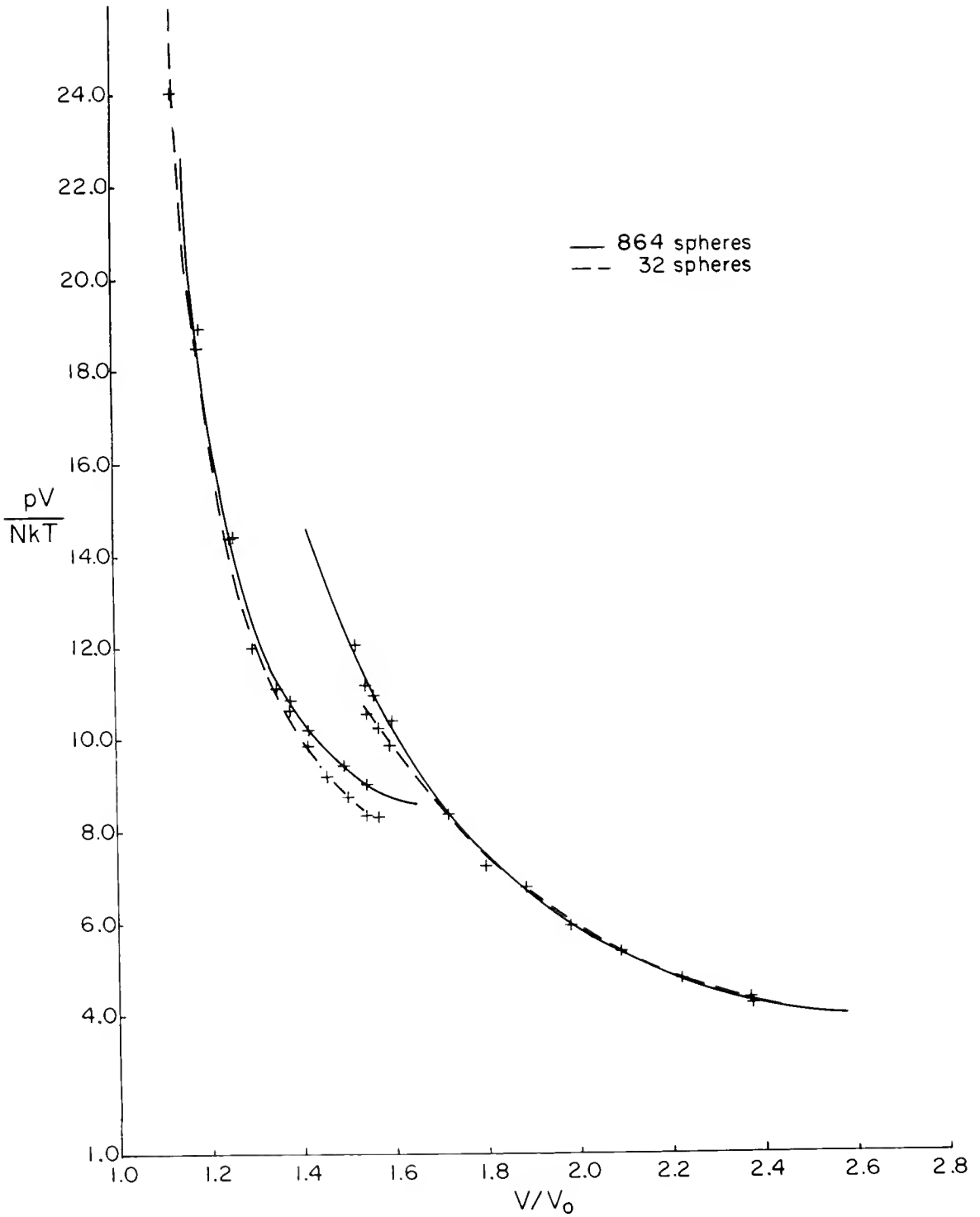

Figure 10. Equation of State for Hard Spheres

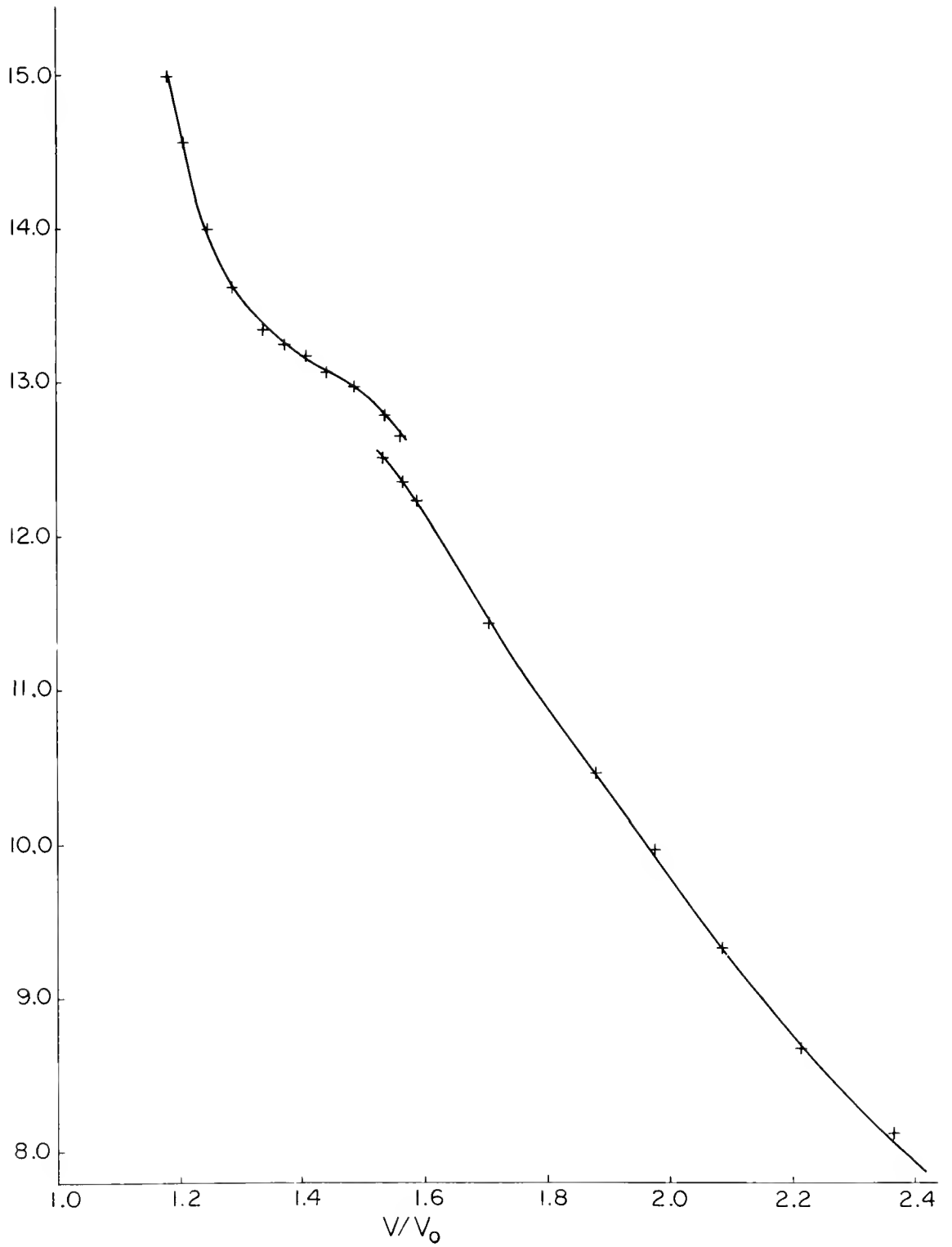

Figure 11. Average Number of Neighbours Out to $1.5d_0$

6. The Phase Transition

In this section the phase transition is discussed in more detail. Reference is made mostly to the three dimensional case but similar comments apply to systems of hard disks also. The graphs of the equation of state for hard disks, Fig. 6, and for hard spheres, Fig. 10 confirm the earlier work of Wood and Alder and Wainwright and leave no doubt of the existence of a phase transition. The phase transition occurs at a density such that $d/d_o \approx 1.16$ where d is the interparticle spacing of nearest neighbours in the regular array and d_o is the particle diameter. This might suggest a phase transition in one dimension at $L/L_o = 1.16$ but as is well known no such transition exists. At high densities the particles are constrained to move about their lattice positions. As the density is decreased and more space is made available there is a tendency for the particles to clump together, leaving a few particles free to move in the system. The phase transition occurs at that density where particles first become free to move. This model explains the high pressure observed at the transition, most of the particles being clumped together give a large value for the radial distribution function at contact. This model of the transition makes it clear why many moves must be made before the transition is observed, since from a more or less regular arrangement many moves are needed to form a clump. If we had a cathode ray tube attached

to our computer we could take pictures to get some confirmation of clumping and to determine the number of particles in a clump. Wainwright and Alder[9] do show some such pictures but they are for only 32 spheres and show motions over several thousand collisions. These pictures do not show evidence of clumping, but they do show that in the fluid phase all the particles tend to move much larger distances than in the solid phase. With so few particles one would hardly expect to see clumps, especially over many collisions where particles could move in and out of a clump. A succession of these pictures shows that the system goes from one phase to the other and back again. Now Wainwright and Alder carry out a dynamical rather than a Monte Carlo calculation and whether this is the reason for the successive phase changes which do not occur in our runs is not known. Certainly the two methods do give the same equation of state[4,8].

Some of the evidence for the clumping model is presented in Table V where the distribution of nearest neighbours is given for a system of 864 hard spheres. As with the radial distribution function the distances are expressed as zone numbers as defined by eq. (3). Note that if A is the nearest neighbour to B, B may not be the nearest neighbour to A since C may be closer in some other direction. Extrapolating the nearest neighbour distribution function one-half zone gives the value at contact and this should be the same as

$g(d_o)$. This has been confirmed approximately in several cases but the extrapolation is quite inaccurate because the curve is so steep. From Table V it is seen that in the solid phase 416 spheres (48%) have their nearest neighbour in the first zone whereas the fluid phase 498 (58%) have their nearest neighbour there, that is the spheres tend to be closer together on the average in the fluid phase.

Zone No.	Solid Phase	Fluid Phase
1	416.3	497.5
2	222.0	209.2
3	110.0	90.5
4	54.7	38.8
5	25.6	16.4
6	12.3	6.8
7	5.2	2.9
8	2.3	1.1
9	1.0	.5
10	.3	.2
11	.2	.1
12	.1	

TABLE V. Nearest Neighbour Distribution Function $V/V_o = 1.511$

Further evidence for the clumping model is provided by examining the average distance of neighbours. Since the NLIST contains the distances of all neighbours lying within a sphere of radius Kd_o expressed as zone numbers, it is a simple matter to add up these distances for each sphere and then to divide the sum by the number of neighbours. This gives an average distance which is also expressed as a zone number. The distribution of these average distances for a system of 864 particles is plotted in Fig. 12

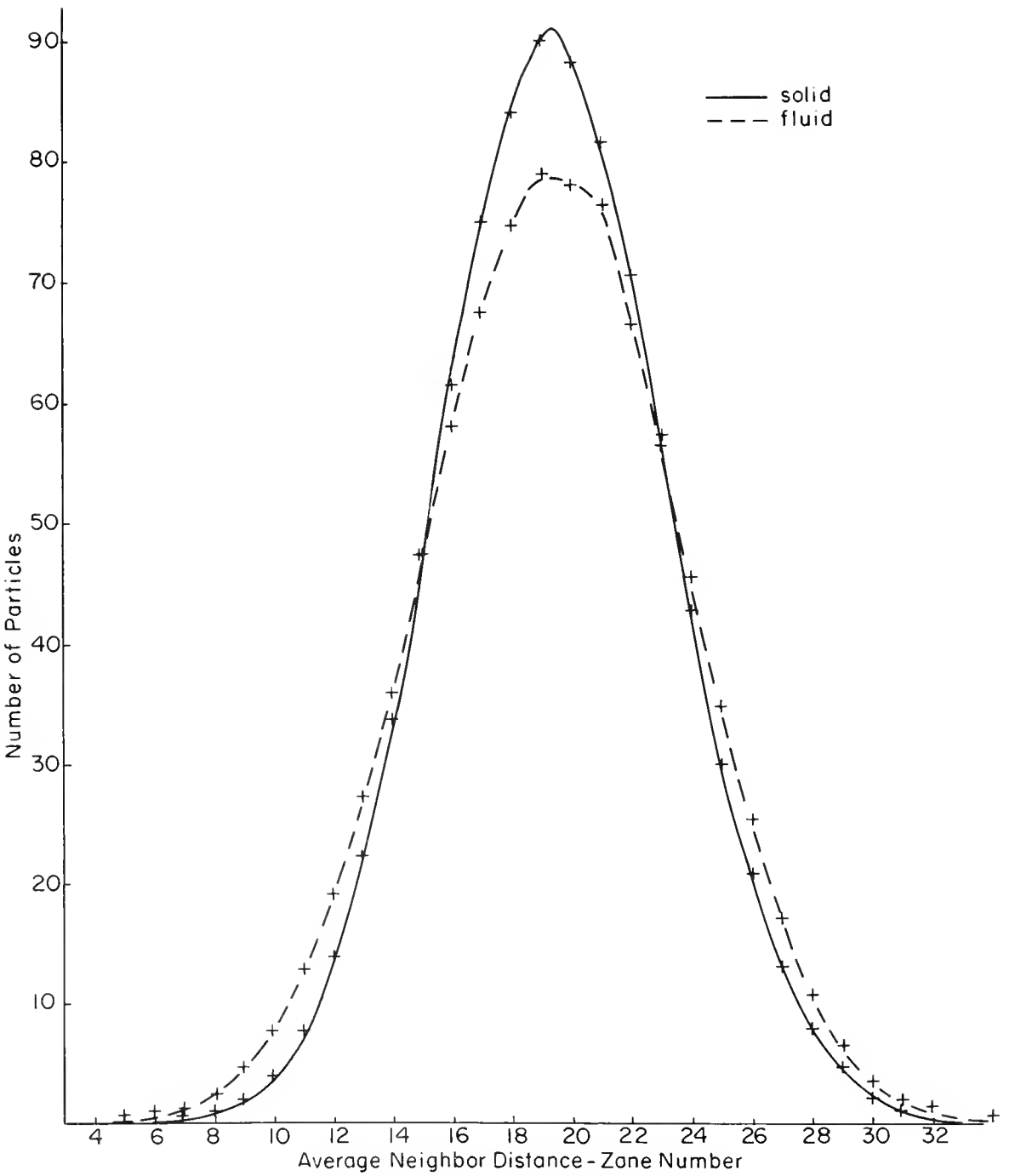

Figure 12. Average Distance of Neighbours (864 Particles)

for both the solid and fluid phases. It is seen that in the fluid phase the curve is flatter than in the solid phase indicating that some spheres have neighbours closer and some have neighbours farther away than in the solid. This is just what would be expected in the clumping model. One might expect a similar effect as far as nearest neighbours are concerned, but the fact that Table V does not exhibit a long tail in the fluid phase indicates that the relatively freely moving particles are situated more or less at the edges of a clump where some neighbour is quite close by. Thus the freedom to move is restricted in direction. Nonetheless, if the clumping model is valid, then in the fluid phase some particles would be expected to move fairly long distances. The distribution of the distance moved (migration lengths) in 50 and in 500 cycles was examined for both 32 and 864 particle systems, and the results are shown in Figures 13 and 14. For 50 cycles the expected effect is not observed, in fact the particles have moved less on the average in the fluid phase. But after 500 cycles the graphs for the fluid phase do have long tails indicating that some particles are indeed able to move long distances and this is in full consonance with the pictures displayed by Wainwright and Alder[9]. The effect is rather more striking than appears in Figure 14 because in the fluid phase there is a smaller probability of making a move (18%) than in the solid phase (24%) and this is a contributing reason for

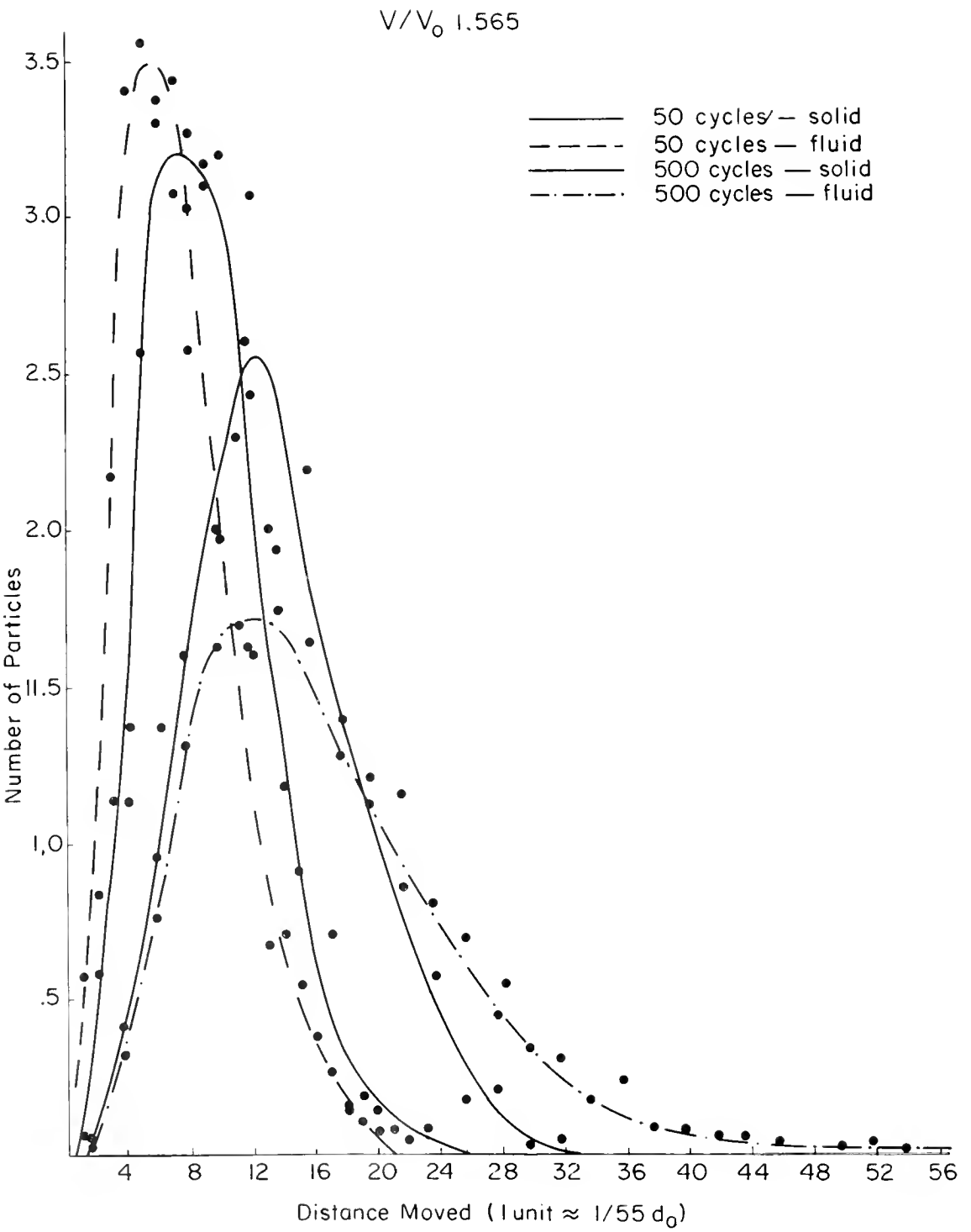

Figure 13. Migration Length - 32 Particles
$V/V_0 = 1.565$

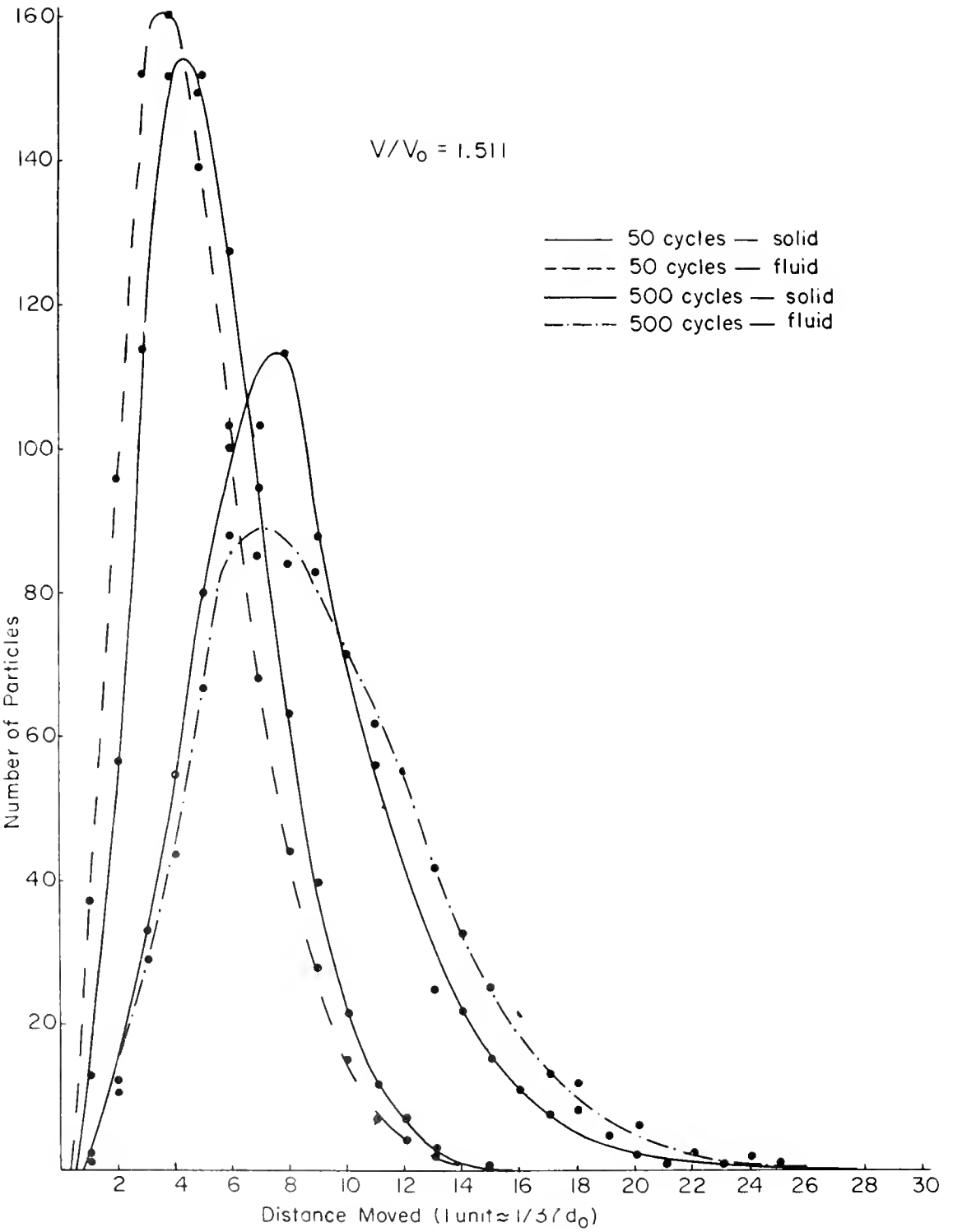

Figure 14. Migration Length - 864 Particles

the absence of a tail after 50 cycles. On our model, though, the particles which move far are not the ones in the clump whose moves are inhibited. What seems to be indicated is that the clumps are not very well defined even for the larger system and that on the average a particle will go from the inside to the outside rather easily. For small systems this is certainly suggested by Wainwright and Alder's pictures. And the implications of the results of imposing a gravitational field to be discussed in the next section also suggest that clumping is a qualitative rather than a quantitative phenomenon.

One other aspect of the transition which is of interest is that it first appears at $V/V_o = 1.539$ for a system of 32 spheres and at $V/V_o = 1.511$ for an 864 particle system. Even ignoring the effect of the periodic boundary which is to keep the particles regularly spaced, we would expect the transition to appear at a higher density for larger systems, because more particles can form a clump leaving more space available for some particles to move freely. If this latter argument were taken seriously there would be far-reaching implications, since for a very large N, say $N \sim 10^{23}$, very large clumps could be formed and as soon as the system density departs from exact close packing enough space could be made available by clumping to permit some particles to move out of their immediate neighbourhoods. Thus the transition for such a system would occur at an extremely high density, perhaps so

high that the transition could never be observed, that is the system is always in what we call the fluid phase. Lest one be tempted to argue that there is only a small change (less than 2%) in the density at which the transition takes place for an increase of more than an order of magnitude in the number of particles, it should be pointed out that both 32 and 864 are very small compared to 10^{23} and to the extent that the boundary conditions play a role the relevant number is not N but $\sqrt[3]{N}$, the average number of particles to a side of the periodic cell.

7. Gravitational Potential

The clumping model has one paradoxical feature which is that clumps occur in the fluid phase even though a clump evokes a picture of a solid. The reason for the designations of the phases as fluid or solid is that from the clumped or fluid phase an increase in volume results in no discontinuities in any observed quantity as the volume gets very large. Similarly from the solid phase, a decrease in volume gives rise to no discontinuities until close packing is reached. In order to study the transition between the two phases and to attempt to obtain a more quantitative description of the transition, we imposed a gravitational field on the system. The field was given the form

$$\phi(x) = sx \qquad x < \tfrac{1}{2}$$
$$\phi(x) = s(1-x) \qquad x > \tfrac{1}{2} \tag{13}$$

where s is a constant expressed in units of kT. This form was chosen to make the field continuous across the periodic boundary. The field was imposed only in one direction, x, and experiments were carried out for both disks and spheres. If the phase transition is first order, then the gravitational field would separate out the two phases, with the heavier phase at the "bottom" and the lighter phase at the "top" of the unit cell. And this separation would be maintained as the field strength s is reduced. Furthermore, if there is a first order effect, we can expect to observe it only in the transition region, since at lower or higher densities the two phases do not coexist. If, on the other hand, the transition is not first order, the two phases will have the same density and we expect to see no difference in the two regions as $s \longrightarrow 0$. Now we do not know a priori (assuming that there is a first order transition) where the interface between the two phases lies. For this reason and because of the difficulty in getting good statistics, the box is divided arbitrarily into two halves, one region for those values of x lying between $1/4$ and $3/4$ (the"top" of the box) and the other for the rest (the "bottom"). We observe the density of particles in each region as the gravitational field is reduced. Fig. 15 shows

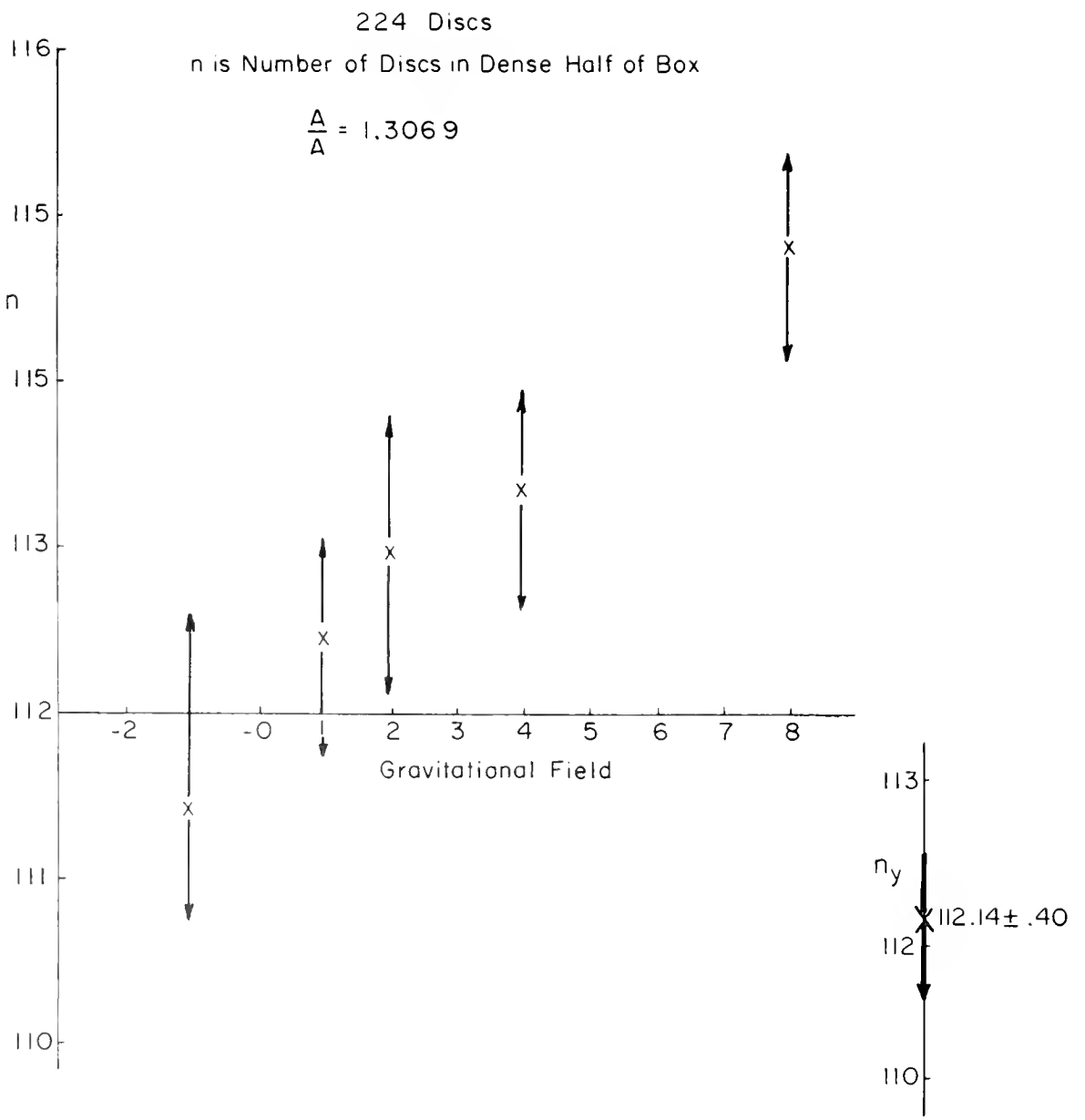
224 Discs
n is Number of Discs in Dense Half of Box
A/A = 1.3069
116
115
n
115
113
112
111
110
-2
-0
1
2
3
4
5
6
7
8
Gravitational Field
113
n_y
112.14± .40
112
110

Figure 15

the results for 224 particles in two dimensions. The abscissa is the field given in units of kT and negative numbers mean simply that the field direction was reversed. The ordinate is the number of particles observed in the dense region -the bottom half of the box. In the absence of the field there will be 112 disks in each half on average. The data were taken consecutively beginning with the largest value of s, that is we began with $s = 8$ and used the output of that run as input for $s = 4$ and so on. Because the statistical fluctuations are large it was necessary to process 50,000 cycles for each value of s and this represents about 12 hours of computing on the IBM-7090. Statistics were recorded every 5000 cycles and the errors shown in Fig. 15 are the maximum and minimum values obtained. Because of the wide fluctuations, a probable error is not indicated, but it would be about one-third the spread shown. During the runs, the density in the y-direction was monitored, again by diving the box into two equal regions. Here the probable error was computed and for one of the regions the number of particles was found to be $112.14 \pm .40$ so the observed value is within one-half of a probable error of 112. The relatively small probable error is not because statistics are better in the y-direction but because the average is calculated over the runs for all values of s. On account of the large fluctuations it is difficult to reach firm conclusions but the indications are that there is no phase

separation. Notice that in projecting the value of n (the number in the bottom half) to $s = 0$ we must not use the results shown for $s = -1$; clearly the values of n at $s = \pm 1$ will be symmetric about $n = 112$. The point at $s = -1$ is included only as a check on the code.

Since the position of the interface if there is a phase separation is not known, it is possible that there really is a separation but that the density is such that most of the particles are in one phase so that the arbitrary division into halves would not exhibit the effect we seek to observe. To test this possibility, the whole calculation was repeated at a slightly lower density, the evidence being that in the first run the system was in the solid phase. The results shown in Fig. 16 are essentially the same as before.

A similar computation was carried out in three dimensions but because of the very long time required to do the kind of study carried out with disks, only a few runs were made and the data were analysed differently. For each run, both the density and the radial distribution function were obtained for each half of the box. Thus the pressure could be calculated separately in each half. In particular we considered three cases, one where the overall density was such that in the absence of the gravitational field the system would be in the solid phase, one case in the transition region and the third in the fluid region of density. These calculations were done for

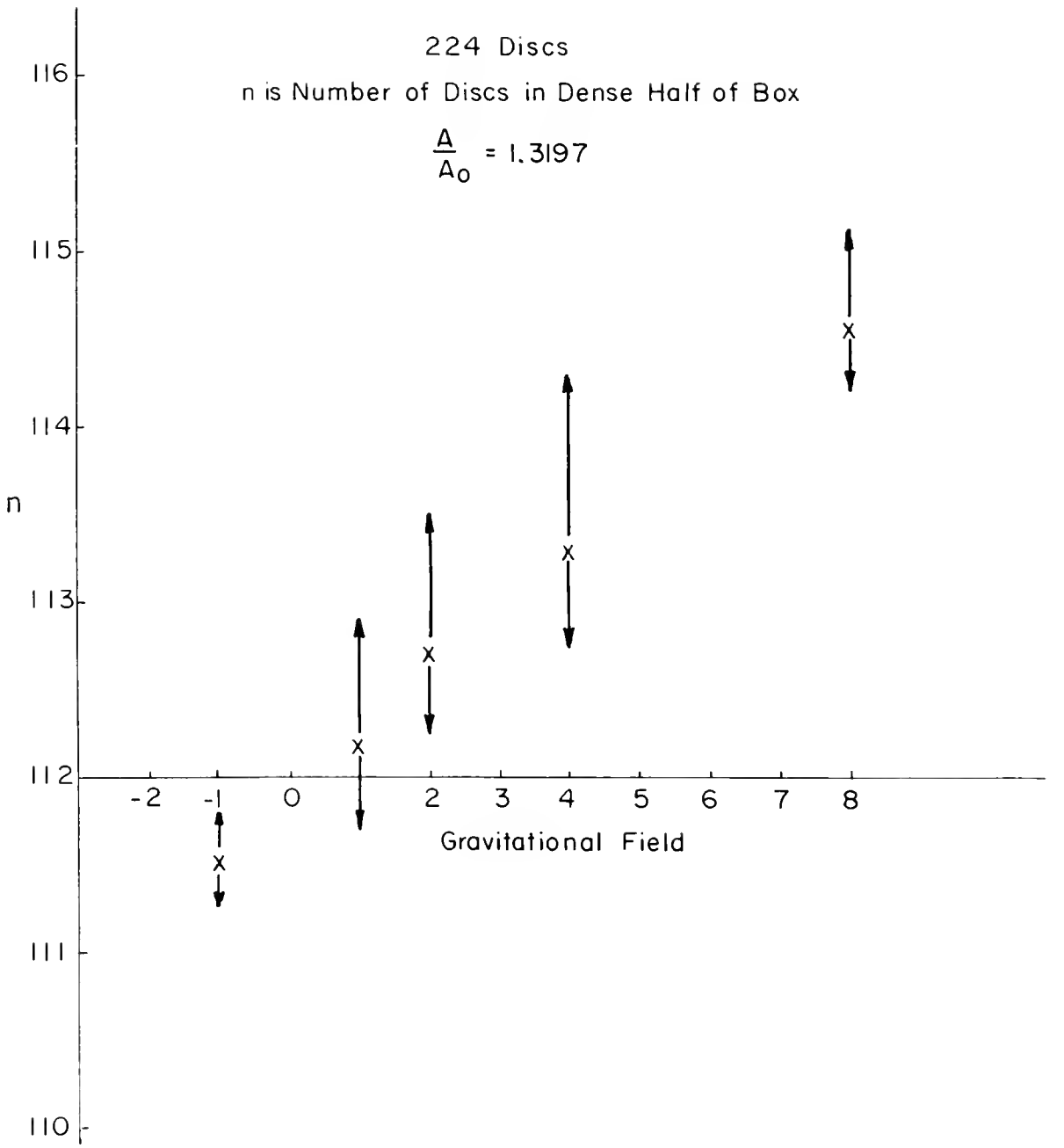
224 Discs
n is Number of Discs in Dense Half of Box
A/A0 = 1.3197
116
115
114
113
112
111
110
n
-2
-1
0
2
3
4
5
6
7
8
Gravitational Field

Figure 16

a few different values of s, the field strength. If there were any tendency for a phase separation then the pressures in the two halves of the box ought to be such as to lie on different branches of the equation of state. This is actually quite strongly to be expected, particularly at the higher field strengths since the effect of the field is to increase the density in one half and decrease it in the other by amounts which bring the average density in each region quite far from the density at which the transition occurs. Some results are shown in Table VI. In column 1 is the average density over the whole system and in column 2 the field strength in units of kT. On the basis of the observed numbers of particles in the bottom half of the box, the density in the dense region is calculated and given in the third column. Columns 4 and 5 give respectively the pressure calculated from the two body distribution function in the bottom half and the pressure read off from the graph of the equation of state, Fig. 10, on the basis of the density given in column 3. Columns 6, 7, and 8 are the same as 3, 4 and 5 but for the top half of the box. The branch of the equation of state from which the pressure in columns 5 and 8 is taken is indicated by a superscript F or S for fluid or solid. We see that both parts of the system always lie on the same branch of the equation of state. This is true even for very large field strengths where it is necessary to extrapolate the equation of state far beyond what is reasonable.

Average $\frac{V}{V_o}$	Field Strength s	Dense Region			Rare Region		
		$\frac{V}{V_o}$	pV/NkT		$\frac{V}{V_o}$	pV/NkT	
			Monte Carlo	From Fig.10		Monte Carlo	From Fig.10
1.493	2	1.440	9.92	9.95^S	1.551	9.29	9.04^S
1.516	2	1.496	12.44	12.48^F	1.538	11.76	11.52^F
1.516	64	1.342	19.8	18.4^F	1.700	10.0	9.30^F
1.540	2	1.535	11.76	11.56^F	1.545	10.94	11.29^F
1.540	32	1.439	14.82	13.98^F	1.652	9.54	9.35^F

TABLE VI. Effect of the Gravitational Field.

There is never any doubt as to which branch of the equation of state should be used to make the comparisons in columns 5 or 8. Consider for example the third line in Table VI, average $V/V_o = 1.516$, $s = 64$. In the dense region the specific volume is 1.342 and the solid branch of the equation of state gives $pV/NkT = 10.58$, which is much too small to agree with the observed value. No cases were run for large field strengths from the solid phase ($V/V_o = 1.493$) because if the equation of state of the solid branch were extrapolated it would merge with the fluid branch and it would be impossible to distinguish the phase on the basis of the pressure.

Examination of Table VI indicates that the effect of the gravitational field is stronger at higher densities. Considering the case $s = 2$, we see that at $V/V_o = 1.540$ the field makes only a small change in the densities in the two regions whereas at $V/V_o = 1.493$ the change is about 4%. The reason for this is not at all clear.

As was the case with disks, the results with spheres in a gravitational field show that there is no tendency for the system to separate into regions having different phases. This is particularly striking since we know that a small system with only 32 particles undergoes the transition and hence in a larger system with 864 spheres we would expect that the two phases can coexist. Starting from the regular lattice at a density in the transition region, a system of 864

particles may persist in the solid phase for several thousand cycles. Once the transition begins to take place, it takes several hundred or even a few thousand cycles before the fluid phase is completely entered into. Perhaps this intermediate situation is one in which the two phases coexist but it is very difficult to arrive at any firm conclusion because the system is not in equilibrium so it is not easy to get meaningful data. Furthermore, the transition has been observed to occur when the system is in a gravitational field and no noticeable tendency has been seen which would indicate that one part of the system undergoes the transition independently of the other.

8. Conclusions

The Monte Carlo experiments with hard core particles have confirmed the work of earlier investigators as to the form of the equation of state and in particular to the existence of a phase transition. Some data have been presented to indicate that the phase transition is associated with a clumping of particles. However, the attempts to separate out the two phases by means of an external gravitational field were not successful. This means that we cannot associate one phase with clumped particles and the other with unclumped ones. Rather clumping must be

considered a more qualitative than quantitative phenomenon and in fact some evidence has already been presented to indicate that it is not possible to tag a particle as being inside or outside a clump. Nonetheless it is certain that some sort of clumping does occur for only in this way could particles move out of their neighbourhoods at densities at which they do so move. That the gravitational field does not separate the phases shows that the transition is not of first order.

With the experience gained in this work at least two lines of further research suggest themselves. One is to consider systems of binary mixtures of particles and some results on such system have already appeared in the literature[12,21]. The other is to consider the effect of adding a short range attractive square well potential to the hard core. Codes have already been written to carry out both these projects and reports of the results obtained will be forthcoming in the near future.

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